Nitirfication Studies in Red Soil

By

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Summary

The rate of nitrate formation by *Nitrobacter agilis* in suspensions of two different types of red soil has been studied. It has been found that with the soil alone, the rate of the oxidation of nitrite to nitrate by the bacterium is about the same as with Fred and Davenport's medium, but when calcium or magnesium carbonate is added to the soil, the rate of nitrite oxidation increases. The addition of sodium carbonate to the soil on the other hand has been found to depress the rate of nitrite oxidation by *Nitrobacter agilis*.

Introduction

All the artificial media employed for the cultivation and growth of *Nitrobacter agilis* contain known constituents in definite amounts, and all the constituents of a particular medium produce a combined effect on the growth of the bacterium. Soil is a complex medium since it is composed of large number of inorganic and organic materials. It is, therefore, natural to expect that the influence of soil on the growth and activity of the bacterium will be different from that of artificial media.

In order to find out the extent of influence of soil on the growth and activity of *Nitrobacter agilis* we undertook a quantitative study of nitrate formation by the bacterium by employing suspensions of soil as media. The chemical composition of the two soils, which have been employed, is given below :

SOIL A

Silica	84·25%
Sesquioxide	8·645%
Phosphoric acid (P_2O_5)	0·05625%
Calcium oxide	0·4704%
Manganese (as oxides)	0·040%
Organic carbon	0·92%
Total nitrogen	0·098%
Ammoniacal nitrogen	0·000236%
Nitrite nitrogen	0·00548%
Nitrate nitrogen	0·00493%
Cation exchange capacity (m.e./100 gm)	21·4

SOIL B

Silica	86·09%
Sesquioxide	5·30%
Phosphoric acid (P_2O_5)	0·0645%
Calcium oxide	0·49%
Manganese (as oxides)	0·025%
Organic carbon	0·76%
Total nitrogen	0·091%
Ammoniacal nitrogen	0·0035%
Nitrite nitrogen	0·000145%
Nitrate nitrogen	0·0021%
Cation exchange capacity (m.e./100 gm)	24·00

Experimental

The following solutions were taken :

Solution A. Sterilized sodium nitrite solution containing one mg nitrogen per ml.

Solution B. Containing all the constituents of Fred and Davenport's medium[1] except sodium nitrite.

For the systematic study, six sets each comprising of four 250 ml conical flasks were taken. In each flask of the first two sets 1·0 g, in each flask of the other two sets 2·0 g and in each flask of the remaining two sets 3·0 g of the soil were taken. In this way the above six sets were split up into three groups, each group comprising of two sets. Into each of the three flasks of every set 0·01, 0·05 and 0·10 g of $MgCO_3$ was added. The fourth flask of each set was left as such with no carbonate. 50 ml distilled water was then added to the contents of each flask. One more flask with 50 ml of the solution B was also taken. 0·2 ml of the solution A was then added to each of the above flasks. All the flasks were sterilized at 15 lb pressure for 15 minutes in an electric autoclave. After sterilization the flasks were allowed to cool, and then 1 ml inoculum of a pure culture of *Nitrobacter agilis* was introduced into each of the flasks ; all the flasks were then kept in an incubator.

Nitrite was estimated in all the flasks of one set of each group after 48, 96, 168, 240 and 360 hrs by Griess–Ilosovay method[2].

Total nitrogen (nitrite + nitrate) was estimated in the flasks of the other set of each group in the beginning and at the end of each experiment by brucine method[3].

Similar experiments were carried out with calcium and sodium carbonates also.

Results and Discussion

The total amount of nitrogen (nitrite + nitrate) remains the same in the beginning and at the end of each experiment as has been found by quantititive determination. This clearly indicates that there is no loss of nitrogen during the microbial oxidation of nitrite, and that all the nitrite which disappears changes only to nitrate.

The results given below in Table 1 show that the oxidation of nitrite is fairly rapid in the medium which contains the soil A alone, and it is only little

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less than that in the Fred and Davenport's medium. It is also evident from the results that the rate of nitrite oxidation decreases with the increase in the amount of the soil added.

TABLE 1

Nitrite oxidation in suspensions containing soil A

Nature of the medium	Nitrite nitrogen left at different intervals of time (in mg)				
	Time in hours				
	48	96	168	240	360
Fred and Davenport's medium.	0·1488	0·0574	0·0044	–	–
1·0 g soil + 50 ml distilled water.	0·1561	0·0893	0·0163	–	–
2·0 g soil + 50 ml distilled water.	0·1634	0·1071	0·0356	–	–
3·0 g soil + 50 ml distilled water.	0·1670	0·1206	0·0494	–	–

In the medium which has only soil B, (Table 2), the nitrite oxidation is more than that in the Fred and Davenport's medium; and further, here unlike soil A the rate of nitrite oxidation increases with increase in the amount of the soil added.

TABLE 2

Nitrite oxidation in suspensions containing soil B

Nature of the medium	Nitrite nitrogen left at different intervals (in mg)				
	Time in hours				
	48	96	168	240	360
Fred and Davenport's medium.	0·1488	0·0574	0·0044	–	–
1·0 g soil + 50 ml distilled water.	0·1343	0·0312	–	–	–
2·0 g soil + 50 ml distilled water.	0·1307	0·0152	–	–	–
3·0 g soil + 50 ml distilled water.	0·1316	0·0131	–	–	–

The addition of calcium carbonate to both the soil media has been found to enhance the rate of nitrification. The greater the amount of soil in the medium, the greater is the amount of $CaCO_3$ needed to produce maximum nitrate formation. The ratio of the soil and $CaCO_3$ which produces maximum nitrite

oxidation in both the soil media is approx. 50 : 1 to 25 : 1. The reason for the increase in the rate of nitrite oxidation must lie in the fact that calcium is an important nutrient element for the bacterium and that the bacterium can also utilize carbonate ions as its source of carbon. Calcium carbonate also serves to neutrilize the acid produced during nitrification and this prevents the medium becoming acid. The higher acidity is not favourable for the growth and activity of *Nitrobacter agilis*.

The addition of $MgCO_3$ to the two media has also been found to enhance the rate of nitrification, but this enhancement is less than that which occurs in presence of $CaCO_3$. The ratio of the soil and $MgCO_3$ which produces maximum nitrification in both the soil media is about 100 : 1 to 40 : 1. The reasons for the beneficial behaviour of $MgCO_3$ are almost the same as have been pointed out in the case of $CaCO_3$; but in the case of $MgCO_3$ these effects are less pronounced. Bomecke[4] reported that *Nitrobacter agilis* would not grow in media from which Mg was omitted and the growth would be less where the amount of Mg is lower than the optimum. This also substantiates that Mg is an essential nutrient for the bacterium.

Unlike $CaCO_3$ and $MgCO_3$ the presence of Na_2CO_3 in both the soil containing media has been found to retard the rate of nitrite oxidation ; and the decrease in the rate is directly proportional to the increase in the amount of Na_2CO_3. The decrease in the rate of nitrite oxidation in the presence of Na_2CO_3 appears to be due to the fact that the latter when present causes dispersion of the soil and that the higher amounts of sodium ions are toxic to the bacterium. The higher pH of the media due to Na_2CO_3 is also unfavourable for the growth and activity of the nitrate-forming bacterium.

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Finite integrals involving product of Bessel functions

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Abstract

The object of the present paper is to evaluate some finite integrals involving product of Bessel functions, by using the result of BAILEY [Some expansion in Bessel functions involving Appell's function F_4, Quart. J. Math, Oxford, 6 (1935), p. 235]

$$x^{\lambda-\mu-\nu} J_\mu(bx) J_\nu(cx) = \frac{2^{\lambda-\mu-\nu} b^\mu c^\nu}{\Gamma(\mu+1)\,\Gamma(\nu+1)} \sum_{n=0}^{\infty} \frac{(\lambda+2n)\,\Gamma(\lambda+n)}{\lfloor n} J_{\lambda+2n}(x) \times$$

$$F_4(-n,\,\lambda+n\,;\,\mu+1,\,\nu+1\,;\,b^2,\,c^2)$$

The integrals obtained are very interesting and include as particular cases some known results.

1. The object of the present paper is to evaluate some finite integrals involving product of Bessel functions. The integrals obtained are very interesting and include as particular cases some known results.

BAILEY [3, p. 235] has shown that

$$x^{\lambda-\mu-\nu} J_\mu(bx) J_\nu(cx) = \frac{2^{\lambda-\mu-\nu} b^\mu c^\nu}{\Gamma(\mu+1)\,\Gamma(\nu+1)} \sum_{n=0}^{\infty} \frac{(\lambda+2n)\,\Gamma(\lambda+n)}{\lfloor n} J_{\lambda+2n}(x) \times$$

(1·1)

$$F_4(-n,\,\lambda+n\,;\,\mu+1,\,\nu+1\,;\,b^2,\,c^2).$$

Multiplying both sides of (1·1) by $f(x)$, then integrating with respect to 'x' from 0 to a and interchanging the order of integration and summation, we get

$$\int_0^a x^{\lambda-\mu-\nu} J_\mu(bx) J_\nu(cx) f(x)\,dx = \frac{2^{\lambda-\mu-\nu} b^\mu c^\nu}{\Gamma(\mu+1)\,\Gamma(\nu+1)} \sum_{n=0}^{\infty} \frac{(\lambda+2n)\,\Gamma(\lambda+n)}{\lfloor n} \times$$

(1·2) $$F_4(-n,\,\lambda+n\,;\,\mu+1,\,\nu+1\,;\,b^2\,c^2) \int_0^a J_{\lambda+2n}(x)\,f(x)\,dx$$

for $R(\lambda+\xi+1)>0$ where $f(x)=0\,(x^\xi)$ for small x.

The change of order of integration and summation is justified by the following conditions, [4, p. 500] ;

(*i*) the series

$$\sum_{n=0}^{\infty} \frac{\lambda+2n)\ \Gamma(\lambda+n)}{\lfloor n} \ J_{\lambda+2n}(x)\ F_4(-n,\ \lambda+n\ ;\ \mu+1,\ \nu+1\ ;\ b^2,\ c^2)$$

is uniformly convergent in $0 \leqslant x \leqslant \beta$, β being arbitrary.

(*ii*) $f(x)$ is a continuous function of x for all values of $x \geqslant x_0 > 0$.

(*iii*) the integral on left converges absolutely, this is so if

$$R(\lambda+\xi+1)>0, \text{ where } f(x)=0(x^{\xi}) \text{ for small } x.$$

2. In this section we shall evaluate some finite integrals with the help of result (1·2).

If we take,

$$f(x) = x^{a-1}\ (a-x)^{\beta-1}\ J_\rho(x)$$

then using (1·2) and evaluating the integral on right with the help of a known result [8, p. 302] we obtain,

$$(2·1) \qquad \int_0^a x^{\lambda-\mu-\nu+a-1}\ (a-x)^{\beta-1}\ J_\mu(bx)\ J_\nu(cx)\ J_\rho(x)\ dx$$

$$= \frac{2^{-\mu-\nu-\rho}\ b^\mu c^\nu\ \Gamma(\beta)}{\Gamma(\mu+1)\ \Gamma(\nu+1)\ \Gamma(\rho+1)} \sum_{n=0}^{\infty} \frac{\Gamma(\lambda+n)\ \Gamma(\lambda+2n\ \rho+a)\ 2^{-2n}\ a^{\lambda+a+\beta+2n+\rho-1}}{\lfloor n\ \Gamma(\lambda+2n)\ \Gamma(\lambda+2n+\rho+\alpha+\beta)} \times$$

$$F_4(-n,\ \lambda+n;\ \mu+1,\ \nu+1\ ;\ b^2,\ c^2) \times$$

$$_4F_5\left[\begin{array}{c} \frac{1}{2}(\lambda+2n+\rho+\alpha),\ \frac{1}{2}(\lambda+2n+\rho+\alpha+1),\ \frac{1}{2}(\rho+1),\ \frac{1}{2}(\rho+2)\ ;\ -a^2/4 \\ \lambda+2n+1,\ \rho+1,\ \lambda+2n+\rho+1,\ \frac{1}{2}(\lambda+2n+\rho+\alpha+\beta),\ \frac{1}{2}(\lambda+2n+\rho+\alpha+\beta+1) \end{array}\right],$$

for $R(\lambda+a+\rho)>0$ and $R(\beta)>0$.

If we take $b=c$, then we get,

$$(2·2) \qquad \int_0^a x^{\lambda+a-1}\ (a-x)^{\beta-1}\ J_\rho(x)\ R\left(\mu+\nu,\ \mu,\ \nu;\ \frac{b^2x^2}{4}\right)\ dx$$

$$= \frac{2^{-\rho}\ \Gamma(\beta)}{\Gamma(\mu+1)\ (\nu+1)\ \Gamma(\rho+1} \sum_{n=0}^{\infty} \frac{\Gamma(\lambda+n)\ \Gamma(\lambda+2n+\rho+\alpha)\ 2^{-2n}\ a^{\lambda+a+\beta+2n+\rho-1}}{\lfloor n\ \Gamma(\lambda+2n)\ \Gamma(\lambda+2n+\rho+\alpha+\beta)} \times$$

$$_4F_3\left(\begin{array}{c} -n,\ \lambda+n,\ \frac{1}{2}(\mu+\nu+1),\ \frac{1}{2}(\mu+\nu+2) \\ \mu+1,\ \nu+1,\ \mu+\nu+1 \end{array} ;\ 4b^2\right) \times$$

$$_4F_5\left(\begin{array}{c} \frac{1}{2}(\lambda+2n+\rho+\alpha),\ \frac{1}{2}(\lambda+2n+\rho+\alpha+1),\ \frac{1}{2}(\rho+1),\ \frac{1}{2}(\rho+2)\ ;\ -a^2/4 \\ \lambda+2n+1,\ \rho+1,\ \lambda+2n+\rho+1,\ \frac{1}{2}(\lambda+2n+\rho+\alpha+\beta),\ \frac{1}{2}(\lambda+2n+\rho+\alpha+\beta+1) \end{array}\right),$$

for $\qquad R(\lambda+a+\rho)>0$ and $R(\beta)>0$,

as when two variables of Appell's fourth hypergeometric function F_4 becomes equal, then it reduces to $_4F_3$ [5, p. 101]

$$(2·3) \qquad F_4(\alpha,\ \beta\ ;\ \gamma,\ \delta\ ;\ x,\ x) = {}_4F_3\left(\begin{array}{c} \alpha,\ \beta,\ \frac{1}{2}(r+\delta-1),\ \frac{1}{2}(r+\delta) \\ \gamma,\ \delta,\ r+\delta-1 \end{array} ;\ 4x\right),$$

and $\dot{R}$-function is defined by AL-SALAM and GARLITZ [1, p. 911], as,

$$(2\cdot4) \qquad R(\lambda, \mu\,;\, \nu,\, x) = \sum_{n=0}^{\infty} \frac{(-1)^n (\lambda+n+1)_n\, x^n}{\lfloor n\, \Gamma(\mu+n+1)\, \Gamma(\nu+n+1)}$$

A result similar to $(2\cdot2)$ has already been obtained by author [7].

Example 2.

If we take

$$f(x) = x^{\rho-1}\,(a-x)^{\,\sigma-1}$$

then using $(1\cdot2)$ and evaluating the integral on right with the help of a known result [6, p. 193] we get,

$$(2\cdot5) \qquad \int_0^a x^{\lambda+\rho-\mu-\nu-1}\,(a-x)^{\sigma-1}\, J_\mu(bx)\, J_\nu(cx)\; dx$$

$$= \frac{b^\mu\, c^\nu\, \Gamma(\sigma)\, 2^{-\mu-\nu}}{\Gamma(\mu+1)\,\Gamma(\nu+1)} \sum_{n=0}^{\infty} \frac{\Gamma(\lambda+n)\,\Gamma(\rho+\lambda+2n)\, 2^{-2n}\, a^{\rho+\sigma+\lambda+2n-1}}{\lfloor n\, \Gamma(\lambda+2n)\,\Gamma(\rho+\sigma+\lambda+2n)} \quad \times$$

$$F_4\left(-n,\,\lambda+n\,;\,\mu+1,\,\nu+1\,;\, b^2,\, c^2\right)\; {}_2F_3\left(\begin{array}{l}\tfrac{1}{2}(\rho+\lambda+2n),\,\tfrac{1}{2}(\rho+\lambda+2n+1)\;;\, -a^2/4\\ \lambda+2n+1,\,\tfrac{1}{2}(\rho+\sigma+\lambda+2n),\,\tfrac{1}{2}(\rho+\sigma+\lambda+2n+1)\end{array}\right),$$

$$R(\lambda+\rho) > 0, \text{ and } R(\sigma) > 0.$$

If $b=c$ then $(2\cdot5)$ reduces to the following form,

$$(2\cdot6) \qquad \int_0^a x^{\lambda+\rho-1}\,(a-x)^{\sigma-1}\, R\left(\mu+\nu,\,\mu,\,\nu\,;\, \frac{b^2\, x^2}{4}\right) dx$$

$$= \frac{\Gamma(\sigma)}{\Gamma(\mu+1)\,\Gamma(\nu+1)} \sum_{n=0}^{\infty} \frac{\Gamma(\lambda+n)\,\Gamma(\rho+\lambda+2n)\, 2^{-2n}\, a^{\rho+\sigma+\lambda+2n-1}}{\lfloor n\, \Gamma(\lambda+2n)\,\Gamma(\rho+\sigma+\lambda+2n)} \quad \times$$

$$_4F_3\left(\begin{array}{l}-n,\,\lambda+n,\,\tfrac{1}{2}(\mu+\nu+1),\,\tfrac{1}{2}(\mu+\nu+2)\;;\, 4b^2\\ \mu+1,\,\nu+1,\,\mu+\nu+1\end{array}\right)\; \times$$

$$_2F_3\left(\begin{array}{l}\tfrac{1}{2}(\rho+\lambda+2n),\,\tfrac{1}{2}(\rho+\lambda+2n+1)\;;\, -a^2/4\\ \lambda+2n+1,\,\tfrac{1}{2}(\rho+\sigma+\lambda+2n),\,\tfrac{1}{2}(\rho+\sigma+\lambda+2n+1)\end{array}\right),$$

$$R(\lambda+\rho) > 0,\; R(\sigma) > 0.$$

Further if $c\to0$, then $(2\cdot6)$ reduces to a known result [6, p. 193] by virtue of a result due to FIELDS and WIMP [8, p. 19].

Example 3.

If we take

$$f(x) = x^{-1}\, J_\rho(a-x),$$

then using $(1\cdot2)$ and evaluating the integral on right [6, p. 354] we get,

$$(2\cdot7) \qquad \int_0^a x^{\lambda-\mu-\nu-1}\, J_\mu(bx)\, J_\nu(cx)\, J_\rho(a-x)\; dx$$

$$= \frac{2^{\lambda-\mu-\nu}\, b^\mu\, c^\nu}{\Gamma(\mu+1)\,\Gamma(\nu+1)} \sum_{n=0}^{\infty} \frac{\Gamma(\lambda+n)}{\lfloor n} J_{\lambda+2n+\rho}\,(a)\, F_4(-n,\,\lambda+n,\,\mu+1,\,\nu+1\,;\, b^2, c^2),$$

for $R(\lambda+\rho) > 0,\; R(\rho) > -1.$

If $b=c$, then (2·7) reduces to the following form,

$$(2·8) \qquad \int_0^a x^{\lambda-1} J_\rho(a-x)\, R\left(\mu+\nu,\ \mu,\ \nu,\ \frac{b^2 x^2}{4} \right) dx$$

$$= \frac{2^\lambda}{\Gamma(\mu+1)\,\Gamma(\nu+1)} \sum_{n=0}^\infty \frac{\Gamma(\lambda+n)}{\underline{|n}} J_{\lambda+2n+\rho}(a)\, {}_4F_3\left(\begin{matrix} -n,\ \lambda+n,\ \frac{1}{2}(\mu+\nu+1),\frac{1}{2}(\mu+\nu+2) \\ \mu+1,\ \nu+1,\ \mu+\nu+1 \end{matrix}\ ;\ 4b^2 \right)$$

for $R(\lambda+\rho)>0$ and $R(\rho)>-1$.

when $c\to 0$ in (2·7) then it reduces to a known result [2, p. 201].

Example 4.

If we start with,

$$f(x)=x^{-1}\,(a-x)^{-1}\,J_\rho(a-x)$$

then using (1·2) and evaluating the integral on right with the help of a known result [6, p. 354 (26)] we get,

$$(2·9) \qquad \int_0^J x^{\lambda-\mu-\nu-1}\,(a-x)^{-1}\,J_\mu(bx)\,J_\rho(a-x)\,dx$$

$$= \frac{2^{\lambda-\mu-\nu}\,b^\mu\,c^\nu\,\rho^{-1}}{\Gamma(\mu+1)\,\Gamma(\nu+1)} \sum_{n=0}^\infty \frac{(\rho+\lambda+2n)\,\Gamma(\lambda+n)}{\underline{|n}}\,J_{\lambda+2n+\rho}(a)\ \times$$

$$F_4(-n,\ \lambda+n\,;\ \mu+1,\ \nu+1\,;\ b^2,\ c^2),$$

for $R(\lambda)>0,\ R(\rho)>0$.

If $b=c$, then (2·9) reduces for the following form,

$$(2·10) \qquad \int_0^a x^{\lambda-1}\,(a-x)^{-1}\,J_\rho(a-x)\,R\left(\mu+\nu,\ \mu,\ \nu,\ \frac{b^2 x^2}{4} \right) dx$$

$$= \frac{2^\lambda\,\rho^{-1}}{\Gamma(\mu+1)\,\Gamma(\nu+1)} \sum_{n=0}^\infty \frac{(\rho+\lambda+2n)\,\Gamma(\lambda+n)}{\underline{|n}}\,J_{\lambda+2n+\rho}(a)\ \times$$

$${}_4F_3\left(\begin{matrix} -n,\ \lambda+n,\ \frac{1}{2}(\mu+\nu+1),\ \frac{1}{2}(\mu+\nu+2) \\ \mu+1,\ \nu+1,\ \mu+\nu+1 \end{matrix}\ ;\ 4\ b^2 \right)$$

for $R(\lambda)>0$ and $R(\rho)>0$.

If $c\to 0$, then (2·9) reduces to a known result [6, p. 354 (27)].

Example 5.

If we take

$$f(x)=x^{2a-1}\,(a^2-x^2)^{\beta-1}\,J_\rho(x)$$

then using (1·2) and evaluating the integral on right with the help of a known result [8, p. 298] we get,

$$(2·11) \qquad \int_0^a x^{\lambda-\mu-\nu+2a-1}\,(a^2-x^2)^{\beta-1}\,J_\mu(bx)\,J_\nu(cx)\,J_\rho(x)\,dx$$

$$= \frac{2^{-\mu-\nu-\rho-1}\,(b^\mu c^\nu\,\Gamma(\beta)}{\Gamma(\mu+1)\,\Gamma(\nu+1)\,\Gamma(\rho+1)} \sum_{n=0}^\infty \frac{\Gamma(\lambda+n)\,\Gamma\{\frac{1}{2}(\rho+\lambda+2n+2a)\}\,a^{\rho+\lambda+2n+2a+2\beta-2}}{\underline{|n}\,\Gamma(\lambda+2n)\,\Gamma\{\frac{1}{2}(\rho+\lambda+2n+2\alpha+2\beta)\}}\ \times$$

$$F_4(-n, \lambda+n; \mu+1, \nu+1; b^2 c^2) \times$$

$${}_3F_4\left(\begin{array}{c} \tfrac{1}{2}(\rho+\lambda+2n+1), \tfrac{1}{2}(\rho+\lambda+2n+2), \tfrac{1}{2}(\rho+\lambda+2n)+\alpha \\ \rho+\lambda+2n, \rho+1, \lambda+2n+1, \tfrac{1}{2}(\rho+\lambda+2n)+\alpha+\beta \end{array}; -a^2\right),$$

$R(\rho+\lambda+2\alpha) > 0$ and $R(\beta) > 0$.

If we take $b = c$ in (2·11) then it reduces to the following form;

$$(2\cdot12) \qquad \int_0^a x^{\lambda+2\alpha-1}(a^2-x^2)^{\beta-1} J_\rho(x) R\left(\mu+\nu, \mu, \nu, \frac{b^2 x^2}{4}\right) dx$$

$$= \frac{2^{-\rho-1}\Gamma(\beta)}{\Gamma(\mu+1)\Gamma(\nu+1)\Gamma(\rho+1)} \sum_{n=0}^\infty \frac{\Gamma(\lambda+n)\,\Gamma\{\tfrac{1}{2}(\rho+\lambda+2n+2\alpha)\}}{\lfloor n\,\Gamma(\lambda+2n)\,\Gamma\{\tfrac{1}{2}(\rho+\lambda+2n+2\alpha+2\beta)\}}\, a^{\rho+\lambda+2n+2\alpha+2\beta-2} \quad \times$$

$$ {}_4F_3\left(\begin{array}{c} -n, \lambda+n, \tfrac{1}{2}(\mu+\nu+1), \tfrac{1}{2}(\mu+\nu+2) \\ \mu+1, \nu+1, \mu+\nu+1 \end{array}; 4 b^2\right) \times$$

$${}_3F_4\left(\begin{array}{c} (\rho+\lambda+2n+1), \tfrac{1}{2}(\rho+\lambda+2n+2), \tfrac{1}{2}(\rho+\lambda+2n+2\alpha) \\ \rho+\lambda+2n, \rho+1, \lambda+2n+1, \tfrac{1}{2}(\rho+\lambda+2n+2\alpha+2\beta) \end{array}; -a^2\right),$$

$R(\rho+\lambda+2n) > 0$ and $R(\beta) > 0$.

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On General Solutions of Polytropes Near the Origin

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Abstract

General solutions of equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 P^{-\frac{n}{n+1}} \frac{dP}{dr} \right) = KP^{\frac{n}{n+1}}$$

for $r<1$ and for all positive values of n, including $n=0$, have been arrived at by the series method, by expressing $P=P_0+cr^2+dr^1+\ldots$ and the solution of the equation for different values of n by expansion as Taylor's series.

The equations governing the equilibrium of gaseous configurations are (Chandrashekhar, S., 1939, Equations 6 and 7, p. 87)

$$\frac{dP}{dr} = -\frac{GM(r)}{r^2}\,\rho\;;\quad \frac{dM(r)}{dr} = 4\pi r^2 \rho \tag{1}$$

eliminating $M(r)$ between the above equations, we have

$$\frac{1}{r^2}\frac{d}{dr}\left(\frac{r^2}{\rho}\frac{dP}{dr} \right) - 4\tau, \rho\, G \tag{2}$$

eliminating ρ by the relation $P = k\rho^{1+1/n}$ we have

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 P^{-\frac{n}{n+1}} \frac{dP}{dr} \right) = -4\pi Gk^{-\frac{2n}{n+1}} P^{\frac{n}{n+1}} \tag{3}$$

(3) is the Lane–Emden equation in terms of r and P.

Solutions of the Lane–Emden equation have generally been considered in $(\xi\,;\,\theta)$=variables. Recently Shambhunath (1966) has shown that r and P are the only suitable variables for the study of the structure of polytropic configurations near the origin as the variables ξ and θ are not defined at the origin. In this paper we shall give a general solution of (3) in the form of a series for $r<1$.

Equation (3) can be written in the symbolic form as

$$P_2 - \frac{n}{n+1}\cdot\frac{P_1^2}{P} + \frac{2P_1}{r} = K\,P^{\frac{2n}{n+1}}, \tag{4}$$

where $K = -4\pi Gk^{-\frac{2n}{n+1}}$

Let us assume a solution of (4) near the origin *i.e.*, $r < 1$ in the form of the series

$$P = P_0 + cr^2 + dr^4 + \ldots \tag{5}$$

where $r_0 = 0$ gives $P = P_0$ and $dP/dr = 0$, giving boundary conditions at the origin, and consequently series contains only terms of even powers in r. By substituting the foregoing series (5) in the equation (4) we get

$$P(2c + 12dr^2 + \ldots) - \frac{n}{n+1}(2cr + 4dr^3 + \ldots)^2 + \frac{2}{r}(2cr + 4dr^3 + \ldots)P$$

$$= K(P_0 + cr^2 + dr^4 + \ldots)^{\frac{3n-1}{n+1}}$$

By substituting for P from (5) and equating the coefficients of like powers of r, we can determine the coefficients c and d. Thus the series including the first three terms is found to be

$$P = P_0 + \frac{K}{6} F_0^{\frac{2n}{n+1}} r^2 + \frac{K}{45} \cdot \frac{n}{n+1} \cdot P_0^{\frac{3n-2}{n+1}} r^4 \tag{A}$$

where K is negative, the terms in (A) are alternatively positive and negative. The expression (A) gives the general solution for all positive values of n including $n = 0$. For the verification of the general solution (A) of equation (4), we proceed to find the solution of (4) for $n = 0, 1, 5$ and verify the results derived therefrom.

Case 1. $n = 0$.

Equation (4) becomes for $n = 0$

$$\frac{d}{dr}\left(r^2 \frac{dP}{dr}\right) = r^2 K \tag{6}$$

Integrating (6) twice we have

$$P = \frac{K}{6} r^2 - \frac{c_1}{r} + c_2$$

where c_1 and c_2 are constants of integration.

The general solution of (6) has a singularity at the origin. If, however, we restrict to solutions which are finite at the origin then $c_1 = 0$ and we have

$$P = c_2 + \frac{K}{6} r^2, \tag{7}$$

where $P = P_0$ for $r = 0$ at the origin, hence $c_2 = P_0$. Thus we have

$$P = P_0 + \frac{K}{6} r^2 \tag{8}$$

above result as given in (8) is also obtained if we put $n = 0$ in the general solution (A).

Case II. $n = 1$,

Equation (4) for $n = 1$, becomes

$$P_2 + \frac{2P_1}{r} - \tfrac{1}{2}\frac{P_1^2}{P} = KP \tag{9}$$

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Since $P = f(r)$ taking the solution of the differential equation (9) by expansion as a Taylor's series, we have

$$P = P_0 + r\left(\frac{dP}{dr}\right)_{r=0} + \frac{r^2}{\lfloor 2}\left(\frac{d_2{}^2 P}{dr^2}\right)_{r=0} + \frac{r^3}{\lfloor 3}\left(\frac{d_3{}^3 P}{dr^3}\right)_{r=0} + \cdots \quad (10)$$

We proceed to determine the values of P_1, P_2, P_3 etc. in (10).

As $r = 0$, $dP/dr = 0$ and $\lim\limits_{r \to 0}\dfrac{P_1}{r} \to P_2$.

Substituting the values of P_1 and P_1/r in (9) we have
$$P_2 = K P_0/3.$$

By successive differentiation of (9) and substituting the values of P_1, P_2 as $r \to 0$ we get $P_3 = 0$, $P_4 = \dfrac{4K^2}{15} P_0$ etc. Hence the first three material terms in Taylor's series (10) give

$$P \doteq P_0\left[1 + \frac{K}{6} r^2 + \frac{K^2}{90} r^4\right] \quad (11)$$

which is exactly the same as will be obtained from the general solution (A) on putting $n = 1$.

Case III. $n = 5$

The equation (4) on putting $n = 5$, becomes

$$P_2 - \frac{5}{6}\frac{P_1{}^2}{P} + \frac{2P_1}{r} = KP^{5/3} \quad (12,$$

Proceeding as before as $r \to 0$, $P_1 = 0$, $P_2 = K/3 . P_0{}^{5/3}$

By differentiating (12) twice and substituting the values of P_1, P_2 etc. we get
$$P_3 = 0 \text{ as } r = 0 \text{ and } P_4 = 4/9 \ K^2 \ P_0{}^{7/3}$$

Substituting the values of P_1, P_2, P_3, P_4 in (10) we have

$$P = P_0 + \frac{K}{6} P_0{}^{5/3} r^2 + \frac{K^2}{54} P_0{}^{7/3} r^4. \quad (13)$$

Again (13) will be the same as will be obtained from the general solution for $n = 5$.

We thus see that the equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 P^{-\frac{n}{n+1}} . \frac{dP}{dr}\right) + K P^{\frac{n}{n+1}}$$

governing the equilibrium of gaseous configuration can be studied in the neighbourhood of the centre for all positive values of n, including $n = 0$. Thus by taking a sufficient number of terms in the series solution (5), we can calculate the values of P for $r < 1$ to any required degree of accuracy. By taking finite number of terms, the series solution (5) can be used to study the structure of polytropic configurations for any value of n.

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Density Distribution in Polytropes

By

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Abstract

In this paper, the general solution of the equation

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \rho^{\frac{1}{n}-1} \frac{d\rho}{dr} \right) = -K \frac{n}{n+1} \rho.$$

for $r<1$ and for all values of n, including $n=0$, have been arrived at by the series method. As an alternative solution, by Taylors series, has also been discussed. For the verification of the general solution arrived at, the actual solution of the general equation for $n=1$ has been fully discussed.

The equations governing the equilibrium of gaseous configuration are (Chandrashekhar, S., 1939, equation 6 and 7, p. 87)

$$\frac{dP}{dr} = -\frac{GM(r)}{r^2} \rho ; \frac{d}{dr} M(r) = 4\pi r^2 \rho \tag{1}$$

Eliminating $M(r)$ in between the above equations, we have

$$\frac{1}{r^2} \frac{d}{dr} \left(\frac{r^2}{\rho} \frac{dP}{dr} \right) = -4\pi G\rho \tag{2}$$

Eliminating P by the relation $P = K\rho^{1+1/n}$, we have

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \rho^{1/n-1} \frac{d\rho}{dr} \right) = -K \frac{n}{n+1} \rho \tag{3}$$

where $K = 4\pi G/k$.

Equation (3) is the Lane–Emden equation in terms of r and which is written in the symbolic form as

$$n \rho_2 - (n-1) \frac{\rho_1^2}{\rho} + \frac{2n}{r} \rho_1 = -K \frac{n^2}{n+1} \rho^{2-1/n} \tag{4}$$

For the solution of (4) we assume a series expansion as for $r<1$ (near the origin)

Let $\qquad \rho = \rho_0{}^n + cr^2\rho_0{}^{n-2} + dr^4 \rho_0{}^{n-4} + \cdots$ $\qquad\qquad$ (5).

where $r=0$ gives $\rho=\rho_0{}^n$ (central density) and $\dfrac{d\rho}{dr}=0$, giving boundary conditions at the origin and consequently the series contains only terms of even powers in r. By substituting the foregoing series (5) in equation (4), we have

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$$n(\rho_0{}^n + cr^2\rho_0{}^{n-2} + dr^4\rho_0{}^{n-4} + \ldots)(2c\rho_0{}^{n-2} + 12dr^2\rho_0{}^{n-4} + \ldots)$$
$$- (n-1)(2cr\,\rho_0{}^{n-2} + 4dr^3\rho_0{}^{n-4} + \ldots)^2 + 2n(2c\rho_0{}^{n-2} + 4dr^2\rho_0{}^{n-4} + \ldots)$$
$$(\rho_0{}^n + cr^2\rho_0{}^{n-2} + dr^4\rho_0{}^{n-4} + \ldots)$$
$$= -\frac{Kn^2}{n+1}[\rho_0{}^n + cr^2\rho_0{}^{n-2} + dr^4\rho_0{}^{n-4} + \ldots)^{3n-1/n}$$

By equating coefficients of like powers of r, we can successively determine the coefficients c and d. Thus

$$c = -\frac{K}{6}\frac{n}{n+1}\cdot\rho_0{}^{n+1} \quad\text{and}\quad d = \frac{K^2}{360}\frac{n(8n-5)}{(n+1)^2}\rho_0{}^{2(n+1)}.$$

Thus the series with the first three terms is found to be

$$\rho = \rho_0{}^n\left[1 - \frac{K}{6}\frac{n}{n+1}\rho_0{}^{n-1}r^2 + \frac{K^2}{360}\frac{n(8n-5)}{(n+1)^2}\rho_0{}^{2(n-1)}r^4\right] \tag{A}$$

Relation (A) shows that for a polytrope of a given index n the density of any point for $r<1$ is a definite sub-multiple of the central density.

As an alternative method for obtaining ρ in terms of r in the neighbourhood of the origin will be obtained by expressing $\rho = f(r)$. Applying Taylor's series for its expansion, we have

$$\rho = \rho_0{}^n + r\left(\frac{d\rho}{dr}\right)_{r=0} + \frac{r^2}{\lfloor 2}\left(\frac{d_2\rho}{dr^2}\right)_{r=0} + \frac{r^3}{\lfloor 3}\left(\frac{d_3\rho}{dr^3}\right)_{r=0} + \ldots \tag{6}$$

For equation (4), for $r=0$, $\rho = \rho_0{}^n$ we have $d\rho/dr = 0$ and $\lim_{r\to 0}\frac{\rho_1}{r} = \rho_2$.

Hence we get $\rho_2 = -\frac{K}{3}\frac{n}{n+1}\rho_0{}^{2n-1}$

By successive differentiation of (4) we get

$$\rho_3 = 0, \quad \rho_4 = \frac{K^2}{15}\cdot\frac{n(8n-5)}{(n+1)^2}\rho_0{}^{3n-2}$$

On substituting the values of ρ_1, ρ_2, ρ_3 and ρ_4 in (6) we have

$$\rho = \rho_0{}^n\left[1 - \frac{K}{6}\frac{n}{n+1}\cdot r^2\rho_0{}^{n-1} + \frac{K^2}{360}\frac{n(8n-5)}{(n+1)^2}r^4\rho_0{}^{2n-2} + \ldots\right] \tag{B}$$

where $\rho = 0$ determines the boundary of the star. We thus see that the equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\rho^{\frac{1-n}{n}}\frac{d\rho}{dr}\right) = -K\frac{n}{n+1}\rho$$

governing the equilibrium of gaseous configuration near the origin can be solved for $r < 1$ for all positive values of polytropes of index n including $n = 0$. Thus by taking a sufficient number of terms in the series of the solution, we can calculate the values of ρ for $r < 1$ to any required degree of accuracy. The equation (A) suggests that there is a strong concentration of mass towards the centre, where the central density for $r = 0$ is $\rho_0{}^n$.

Determination of Mass.—The mass $M(r)$ interior to r is given by

$$M(r) = \int_0^R 4\pi r'\rho\,dr.$$

where R is the radius of the gas sphere,

$$= 4\pi\rho_0{}^n \int_0^R r^2 \left(1 - \frac{K}{6} \cdot \frac{n}{n+1} \, r^2 \, \rho_0{}^{n-1} + \frac{K^2}{360} \, \frac{n(8n-5)}{(n+1)^2} \, r^4 \rho_0{}^{2n-2} + \ldots \right) dr$$

$$= 4\pi\rho_0{}^n \left[\frac{r^3}{3} - \frac{K}{6} \cdot \frac{n}{n+1} \, \rho_0{}^{n-1} \frac{r^5}{5} + \frac{K^2}{360} \cdot \frac{n(8n-5)}{(n+1)^2} \, \frac{r^7}{7} \cdot \rho_0{}^{2n-2} + \ldots \right]^R$$

Hence the total mass of the configuration.

$$= 4\pi R^3 \rho_0{}^n \left[\frac{1}{3} - \frac{K}{6} \, \frac{n}{n+1} \, \rho_0{}^{n-1} \cdot \frac{R^2}{5} + \frac{K^2}{360} \, \frac{n(8n-5)}{(n+1)^2} \, \rho_0{}^{2n-2} \, \frac{R^4}{7} + \ldots \right]$$

Let ρ_m denote the mean density of the matter interior to r then

$$\rho_m = \frac{M(r)}{\frac{4}{3}\pi r^3} = \rho_0 \left[1 - \frac{K}{10} \cdot \frac{n}{n+1} \, \rho_0{}^{n-1} \, r^2 + \frac{K^2}{840} \, \frac{n(8n-5)}{(n+1)^2} \, \rho_0{}^{2n-2} \cdot r^4 + \ldots \right]$$

Relation (8) shows that for a polytrope of a given index n, the mean density is a sub-multiple of the central density and for $n=1$, we have the mean density as given by (9)

$$\rho_m = \rho_0 \left[1 - \frac{K}{20} \, r^2 + \frac{K^2}{1120} \, r^4 \ldots \right] \tag{9}$$

For the verification of the series solution (A) we solve the general equation (3) for $n=1$. The general equation (3), for $n=1$ becomes

$$\frac{d_2\rho}{dr^2} + \frac{2}{r} \, \frac{d\rho}{dr} + \frac{K}{2} \, \rho = 0$$

By the method of the removal of the first derivative (Normal form) putting $\rho = uv$, we get

$$u = 1/r, \; v = \rho_0 \, \frac{\sin \sqrt{\frac{K}{2}} r}{\sqrt{\frac{K}{2}}}$$

Hence we get

$$\rho = \rho_0 \cdot \sin \sqrt{\frac{K}{2}} r \; \Big/ \sqrt{\frac{K}{2}} \, r.$$

which is a general solution of (3) for $n = 1$. If r is small, we get an expansion of

$$\sin \sqrt{\frac{K}{2}} r \; \Big/ \sqrt{\frac{K}{2}} r \, ;$$

Hence,

$$\rho = \rho_0 \left[1 - \frac{K}{12} r^2 + \frac{K}{480} \, r^4 - \ldots \right]$$

which corresponds with (A) for $n = 1$.

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On some results involving H-function on Fox

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Abstract

The present paper is in continuation of an earlier one by the author investigating further properties of H-Function of Fox. An integral involving H-Function and Appell's function F_1 has been established besides other results from which the results recently obtained by Saxena (10, p. 47), Sharma (12, pp. 73-74) and Rathie [8, p. 114(6)] can be deduced as particular cases.

1. Introduction : The present paper is in continuation of an earlier one (9) by the author investigating further properties of H-Function of Fox [4, p 408(52)] which following Gupta [5, p. 98(4)], we define as

(1·1)
$$H_{p,q}^{m,n}\left[x \left| \begin{array}{c} (a_p, e_p) \\ (b_q, f_q) \end{array}\right.\right] \equiv H_{p,q}^{m,n}\left[x \left| \begin{array}{c} (a_1, e_1), \ldots, (a_p, e_p) \\ (b_1, f_1), \ldots, (b_q, f_q) \end{array}\right.\right]$$

$$= \frac{1}{2\pi i} \int_L \frac{\prod\limits_{j=1}^{m} \Gamma(b_j - f_j \cdot s) \prod\limits_{j=1}^{n} \Gamma(1 - a_j + e_j \cdot s)}{\prod\limits_{j=m+1}^{q} \Gamma(1 - b_j + f_j \cdot s) \prod\limits_{j=n+1}^{p} \Gamma(a_j - e_j \cdot s)} \cdot x^s \, ds$$

p, q, n, m are integers satisfying $o \leqslant n \leqslant p, 1 \leqslant m \leqslant q$; $e_j, (j = 1, 2, \ldots, p)$;

$f_j, (j = 1, 2, \ldots, q)$ are positive numbers and $a_j, (j = 1, \ldots, p)$;

$b_j, (j = 1, \ldots, q)$ are complex numbers such that

(1·2)
$$e_j (b_h + r) \neq f_h (a_j - 1 - k)$$

$r = 0, 2, 3, \ldots \ldots$; $\qquad$ $k = 0, 1, 2, 3, \ldots \ldots$;

$h = 1, 2, 3, \ldots, m$; $\qquad$ $j = 1, 2, 3, \ldots, n$.

and L is a contour of Barnes type such that the poles of $\Gamma(b_j - f_j \cdot s)$, $(j = 1, 2, \ldots, m)$ lie to the right and those of $\Gamma(1 - a_j + e_j \cdot s)$, $(j = 1, 2, \ldots, n)$ to the left of the contour. Such a contour is possible on account of (1·2).

The following results, believed to be new, have been obtained in this note :

$$(a) \int_0^\infty t^{r-1} H_{s,q}^{m,n}\left[\alpha t \left| \begin{array}{c} (a_1, e_1), \ldots, (a_s, e_s) \\ (b_1, f_1), \ldots, (b_q, f_q) \end{array}\right.\right] H_{\gamma,\delta}^{\alpha,\beta}\left[(b+t) \left| \begin{array}{c} (c_1, h_1), \ldots, (c_\gamma, h_\gamma) \\ (d_1, l_1), \ldots, (d_\delta, l_\delta) \end{array}\right.\right] dt.$$

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$$= \sum_{r=0}^{\infty} \frac{(-1)^r \, b^r}{\lfloor r} \times$$

$$\times H^{\beta+m,\, a+n+1}_{\delta+s+1,\, q+\gamma+1} \left[\alpha \left| \begin{array}{l} (1-\sigma,1),\, (a_1,e_1),\, \ldots,\, (a_n,e_n),\, (1-d_1-\sigma l_1+rl_1,l_1),\, \ldots, \\ (1-d_\delta-rl_\delta+rl_\delta,l_\delta),\, (a_{n+1},e_{n+1}),\, \ldots,\, (a_s,e_s) \\ (b_1,f_1),\, \ldots,\, (b_m,f_m),\, (1-c_1-\sigma h_1+rh_1,\, h_1),\, \ldots, \\ (1-c_\gamma-\sigma h_\gamma+rh_\gamma,h_\gamma),(1+r-\sigma,1),(b_{m+1},f_{m+1}),\ldots,(b_q,f_q) \end{array} \right. \right]$$

provided $\quad \lambda = \sum_{j=1}^{n} (e_j) - \sum_{j=n+1}^{s} (e_j) + \sum_{j=1}^{m} (f_j) - \sum_{j=m+1}^{q} (f_j) > 0,$

$$|\arg(\alpha)| < \tfrac{1}{2}\lambda\pi, \quad |\arg(b)| < \frac{\pi}{2},$$

$$\mu = \sum_{j=1}^{\beta} (h_j) - \sum_{j=\beta+1}^{\gamma} (h_j) + \sum_{j=1}^{a} (l_j) - \sum_{j=a+1}^{\delta} (l_j) - 1 > 0,$$

$$R\left[\sigma + \min_{1 \le j \le m} \frac{b_j}{f_j} \right] > 0,$$

$$\left[\frac{1 - \max R(a_j)}{e_j} \right]_{0 \le j \le n} + \left[\frac{1 - \max R(c_j + \sigma h_j - h_j)}{h_j} \right]_{1 \le j \le \beta} > 1,$$

$e_0 = 1,\quad a_0 = 1 - \sigma,$ and the series on the right is absolutely convergent.

(b) $\quad \displaystyle\int_0^{\infty} x^{\lambda-1} K_\nu(l\,x)\, K_\rho(c\,x)\, H^{m,\,n}_{p,\,q} \left[\frac{\mu}{x^\sigma} \left| \begin{array}{l} (a_1,e_1),\, \ldots,\, (a_p,e_p) \\ (b_1,f_1),\, \ldots,\, (b_q,f_q) \end{array} \right. \right] dx$

$$= \sum_{\nu,\,-\nu} \sum_{r=0}^{\infty} \frac{\pi \cdot 2^{\lambda-3} \cdot l^{2r+\nu}}{\lfloor r \cdot \sin(-\nu\pi)\, \Gamma(r+\nu+1)\, c^{\lambda+2r+\nu}} \times$$

$$\times H^{m+2,\,n}_{p,\,q+2} \left[\mu \left(\frac{c}{2} \right)^\sigma \left| \begin{array}{l} (a_1,e_1),\, \ldots\ldots\ldots\ldots,\, (a_p,e_p) \\ \left(\frac{\lambda+\nu+\rho}{2}+r,\, \frac{\sigma}{2} \right),\, \left(\frac{\lambda+\nu-\rho}{2}+r,\, \frac{\sigma}{2} \right)(b_1,f_1),\ldots,(b_q,f_q) \end{array} \right. \right]$$

where $\quad R\left\{ \lambda \pm \nu \pm \rho + \frac{\sigma(1-a_j)}{e_j} \right\} > 0,\ R(c \pm l) > 0,$

$$\gamma = \sum_{j=1}^{n} (e_j) - \sum_{j=n+1}^{p} (e_j) + \sum_{j=1}^{m} (f_j) - \sum_{j=m+1}^{q} (f_j) \geqslant 0,$$

$|\arg(\mu)| < \tfrac{1}{2}\gamma\pi.$

(c) $\int_0^\infty y^{\nu \cdot a - \frac{1}{2}} \; H^{n+1, \, m+1}_{q+2, \, p+2} \left[\left(\frac{1}{\lambda}\right)^{\frac{1}{\gamma}} \cdot \frac{2}{y} \; \middle| \; \begin{array}{l} \left(1-b_1, \frac{f_1}{\gamma}\right), \ldots, \left(1-b_m, \frac{f_m}{\gamma}\right), \left(\frac{1}{4} - \frac{\nu}{2} - \frac{a}{2}\right) \\ \left(\frac{1}{4} + \frac{\nu}{2} - \frac{a}{2}, \frac{1}{2}\right), \left(1-b_{m+1}, \frac{f_{m+1}}{\gamma}\right), \ldots, \left(1-b_q, \frac{f_q}{\gamma}\right) \\ \left(\frac{1+\rho+\nu}{2}, \frac{\lambda_1}{\gamma}\right), \left(1-a_1, \frac{e_1}{\gamma}\right), \ldots, \left(1-a_p, \frac{e_p}{\gamma}\right) \\ \left(\frac{1+\rho-\nu}{2}, \frac{\lambda_2}{\gamma}\right) \end{array} \right]$

$$\times F_4 \left[A, B; 1+\nu, 1+\sigma; -\frac{y^2}{l^2}, \frac{a^2}{l^2} \right] dy$$

$$= \frac{l^{\nu - a + \frac{1}{2}} \Gamma(1+\nu) \cdot \gamma}{2 \, \Gamma(A) \, \Gamma(B)} \cdot \sum_{r=0}^\infty \frac{\left(\frac{a}{l}\right)^{2r}}{\underline{r} \, (1+\sigma)_r} \times$$

$$\times H^{m+2, \, n+1}_{p+2, \, q+2} \left[\lambda \left(\frac{l}{2}\right)^\gamma \; \middle| \; \begin{array}{l} \left(\frac{1-\rho-\nu}{2}, \lambda_1\right), (a_1, e_1), \ldots, (a_p, e_p), \left(\frac{1-\rho+\nu}{2}, \lambda_2\right) \\ \left(A - \frac{\nu - a + \frac{1}{2}}{2} + r, \frac{\gamma}{2}\right), \left(B - \frac{\nu - a + \frac{1}{2}}{2} + r, \frac{\gamma}{2}\right), (b_1, f_1), \\ \ldots, (b_q, f_q) \end{array} \right]$$

where $R(l \pm a) > 0$, $0 \leqslant n \leqslant p$, $1 \leqslant m \leqslant q$,

$$\delta = \sum_{j=1}^n (e_j) - \sum_{j=n+1}^p (e_j) + \sum_{j=1}^m (f_j) - \sum_{j=m+1}^q (f_j) + \lambda_1 - \lambda_2 > 0,$$

$$|\arg(\lambda)| < \tfrac{1}{2} \delta \pi, \; R\left(\nu - \alpha + \tfrac{1}{2} + \gamma \min \frac{b_j}{f_j}\right) > 0,$$
$$1 \leqslant j \leqslant m$$

$$R\left\{ a + 2A - \nu - \tfrac{1}{2} + \frac{\gamma(1 - \max a_j)}{e_j} \right\} > 0,$$
$$0 \leqslant j \leqslant n$$

$$R\left\{ \alpha + 2B - \nu - \tfrac{1}{2} + \frac{\gamma(1 - \max a_j)}{e_j} \right\} > 0, \; e_0 = \lambda_1, \; a_0 = \frac{1 - \rho - \nu}{2}.$$
$$0 \leqslant j \leqslant n$$

(d)
$$\sum_{\nu, \, -\nu} \; \sum_{r=0}^\infty \frac{\pi^{\frac{1}{2}} \operatorname{cosec}(-2\nu\pi)}{\underline{r} \, \Gamma(2\nu + 1 + r)} \times$$

$$\times H^{m+2, \, n}_{p, \, q+2} \left[z \; \middle| \; \begin{array}{l} (a_1, 2e_1), \ldots \ldots \ldots, (a_p, e_p) \\ (a+\nu+r, \lambda), (\beta+\nu+r, \lambda), (b_1, f_1), \ldots, (b_q, f_q) \end{array} \right]$$

$$= 2^{1-a-\beta} H^{m+4, \, n}_{p+2, \, q+4} \left[4 \cdot \lambda z \; \middle| \; \begin{array}{l} (a_1, e_1), \ldots, (a_p, e_p), \left(\frac{a+\beta}{2}, \lambda\right), \left(\frac{a+\beta+1}{2}, \lambda\right) \\ (a+\nu, \lambda), (a-\nu, \lambda), (\beta+\nu, \lambda), (\beta-\nu, \lambda), (b_1, f_1), \\ \ldots, (b_q, f_q) \end{array} \right]$$

where
$$R\left(1 - \alpha - \beta + 2\lambda \min \frac{b_j}{f_j}\right) > 0.$$
$$1 \leqslant j \leqslant m$$

$$R(1 \pm 2\nu) > |R(\alpha - \beta)|, \quad 1 \pm 2\nu \neq 0, -1, -2, -3, \ldots.$$

It may be remarked here that results recently obtained by Saxena (10, p. 47), Sharma (12, pp. 73, 74) and Rathie { 8, p, 114(6) } may be derived as particular cases of these results.

2. The following results shall be required in our inversigations [6]:

$$(2\cdot1) \quad x^\sigma H^{m,\,n}_{p,\,q}\left[x \left|\begin{array}{l}(a_1, e_1), \ldots, (a_p, e_p)\\(b_1, f_1), \ldots, (b_q, f_q)\end{array}\right.\right]$$

$$= H^{m,\,n}_{p,\,q}\left[x \left|\begin{array}{l}(a_1 + \sigma e_1, e_1), \ldots\ldots, (a_p + \sigma e_p, e_p)\\(b_1 + \sigma f_1, f_1), \ldots, (b_q + \sigma f_q, f_q)\end{array}\right.\right]$$

$$(2\cdot2) \quad H^{m,\,n}_{p,\,q}\left[x^{-1} \left|\begin{array}{l}(a_1, e_1), \ldots, (a_p, e_p)\\(b_1, f_1), \ldots, (b_q, f_q)\end{array}\right.\right]$$

$$= H^{n,\,m}_{q,\,p}\left[x \left|\begin{array}{l}(1 - b_1, f_1), \ldots, (1 - b_q, f_q)\\(1 - a_1, e_1), \ldots, (1 - a_p, e_p)\end{array}\right.\right]$$

$$(2\cdot3) \quad \int_0^\infty H^{m,\,n}_{p,\,q}\left[a\,x \left|\begin{array}{l}(a_1, e_1), \ldots, (a_p, e_p)\\(b_1, f_1), \ldots, (b_q, f_q)\end{array}\right.\right] H^{k,\,l}_{r,\,t}\left[x \left|\begin{array}{l}(c_1, h_1), \ldots, (c_r, h_r)\\(d_1, u_1), \ldots, (d_t, u_t)\end{array}\right.\right] dx$$

$$= H^{l+m,\,n+k}_{p+t,\,q+r}\left[a \left|\begin{array}{l}(a_1, e_1), \ldots, (a_n, e_n), (1 - d_1 - u_1, u_1), \ldots, (1 - d_t - u_t, u_t),\\ \qquad\qquad\qquad (a_{n+1}, e_{n+1}), \ldots, (a_p, e_p)\\(b_1, f_1), \ldots, (b_m, f_m), (1 - c_1 - h_1, h_1), \ldots, (1 - c_r - h_r, h_r)\\ \qquad\qquad\qquad (b_{m+1}, f_{m+1}), \ldots, (b_q, f_q)\end{array}\right.\right]$$

where
$$\gamma = \sum_{j=1}^{n}(e_j) - \sum_{j=n+1}^{p}(e_j) + \sum_{j=1}^{m}(f_j) - \sum_{j=m+1}^{q}(f_j) > 0,$$

$$|\arg(a)| < \tfrac{1}{2}\gamma\pi,$$

$$\left[\min R\left(\frac{d_j}{u_j}\right)\right] + \left[\min R\left(\frac{b_j}{f_j}\right)\right] + 1 > 0,$$
$$1 \leqslant j \leqslant k \qquad\qquad 1 \leqslant j \leqslant m$$

$$\left[\frac{1 - \max R(a_j)}{e_j}\right] + \left[\frac{1 - \max R(c_j)}{h_j}\right] > 1,$$
$$1 \leqslant j \leqslant n \qquad\qquad 1 \leqslant j \leqslant l$$

$$\gamma' = \sum_{j=1}^{l}(h_j) - \sum_{j=l+1}^{r}(h_j) + \sum_{j=1}^{k}(u_j) - \sum_{j=k+1}^{t}(u_j) > 0,$$

(2·4)
$$k_\mu\{x^{\lambda-2} K_\sigma(a\,x)\,f(x)\,;\,p\}$$

$$= \sum_{\sigma,\,-\sigma} \frac{2^{\lambda-3}\,a^\sigma\,\Gamma(-\sigma)}{p^{\lambda+\nu+\sigma-\frac{1}{2}}\,\Gamma(1+\nu)}\;\Gamma_*\{\tfrac{1}{2}(\lambda+\sigma+\nu\pm\mu)\}\times$$

$$\times \int_0^\infty y^{\nu+\frac{1}{2}}\,H_\nu\{f(x)\,;\,y\}\,F_4\left[\frac{\lambda+\sigma+\nu-\mu}{2},\;\frac{\lambda+\sigma+\nu+\mu}{2};\;1+\nu,1+\sigma;\;-\frac{y^2}{p^2},\frac{a^2}{p^2}\right]dy$$

where
$$k_\mu\{f(x)\,;\,p\} = \int_0^\infty (p\,x)^{\frac{1}{2}}\,K_\mu(p\,x)\,f(x)\,dx\,;$$

$$H_\nu\{f(x)\,;\,y\} = \int_0^\infty (x\,y)^{\frac{1}{2}}\,J_\nu(x\,y)\,f(x)\,dx\,;$$

$f(x)$, $H_\nu\{f(x)\,;\,y\}$ belong to $L(0,\infty)$, $R(\lambda\pm\mu+\nu\pm\sigma)>0$, $R(\nu+\frac{1}{2})>0$, $R(p+a)>0$, and $\Gamma_*(a\pm b)$ is used to denote the product $\Gamma(a+b)\,\Gamma(a-b)$.

(2·5)
$$H_\nu\left\{x^\alpha\,H^{n+1,\,m}_{q,\,p+2}\times\right.$$

$$\times\left[\frac{x^\gamma}{\lambda}\left|\begin{array}{l}(1-b_1,f_1),\,\ldots\ldots\ldots\,,\,(1-b_q,f_q)\\ \left(\frac{1+\rho+\nu}{2},\lambda_1\right),\,(1-a_1,e_1),\,\ldots\,,\,(1-a_p,e_p),\,\left(\frac{1+\rho+\nu}{2},\lambda_2\right)\end{array}\right]\,;\,y\right\}$$

$$= \frac{2^{\alpha+\frac{1}{2}}}{\gamma.y^{\alpha+1}}\,H^{n+1,\,m+1}_{q+2,\,p+2}\times$$

$$\times\left[\left(\frac{1}{\lambda}\right)^{\frac{1}{\gamma}}.\frac{2}{y}\left|\begin{array}{l}\left(1-b_1,\dfrac{f_1}{\gamma}\right),\,\ldots\,,\,\left(1-b_m,\dfrac{f_m}{\gamma}\right),\,(\tfrac{1}{4}-\tfrac{\nu}{2}-\tfrac{\alpha}{2},\tfrac{1}{2}),\\[4pt] (\tfrac{1}{4}+\tfrac{\nu}{2}-\tfrac{\alpha}{2},\tfrac{1}{2}),\,\left(1-b_{m+1},\dfrac{f_{m+1}}{\gamma}\right),\,\ldots\,,\,\left(1-b_q,\dfrac{f_q}{\gamma}\right)\\[6pt] \left(\dfrac{1+\rho+\nu}{2},\dfrac{\lambda_1}{\gamma}\right),\,\left(1-a_1,\dfrac{e_1}{\gamma}\right),\,\ldots\,,\,\left(1-a_p,\dfrac{e_p}{\gamma}\right),\,\left(\dfrac{1+\rho-\nu}{2},\dfrac{\lambda_2}{\gamma}\right)\end{array}\right]$$

where
$$R(\alpha+\nu)+\frac{\gamma}{e_j}\{1-\max R(a_j)\}+\tfrac{3}{2}>0,\quad e_0=\lambda_1,\;a_0=\frac{1-\rho-\nu}{2},$$
$$0\leqslant j\leqslant n$$

$$R\left(\alpha-\gamma\,\min\,\frac{b_j}{f_j}\right)<0,$$
$$1\leqslant j\leqslant m$$

$$\delta = \sum_{j=1}^m (f_j) - \sum_{j=m+1}^q (f_j) + \sum_{j=1}^n (e_j) - \sum_{j=n+1}^p (e_j) + \lambda_1 - \lambda_2 > 0,$$
$$|\arg(\lambda)| < \tfrac{1}{2}\,\delta\,\pi.$$

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Here (2·5) is a particular case of a Theorem on H–Functions (9) while (2.4) is given by Sharma (11, p. 112).

We shall also use the conventional notation $\phi(p) \doteqdot g(t)$ to denote the relation

$$\phi(p) = p \int_0^\infty e^{-pt}\, g(t)\, dt.$$

3. Now we set about proving the results (a), (b), (c) and (d) of Art. 1.

Proof of (a) :

From Gupta [5 ; p. 99 result (7)] if we take

$$\phi_1(p) \doteqdot p^{1-\sigma}\ H^{m,\,n+1}_{s+1,\,q}\left[\frac{a}{p}\,\middle|\,\begin{matrix}(1-\sigma,\,1),\,(a_1,\,e_1),\,\ldots,\,(a_s,\,e_s)\\ (b_1,f_1),\,\ldots,\,(b_q,f_q)\end{matrix}\right]$$

$$\doteqdot t^{\sigma-1}\ H^{m,\,n}_{s,\,q}\left[\,at\,\middle|\,\begin{matrix}(a_1,\,e_1),\,\ldots,\,(a_s,\,e_s)\\ (b_1,f_1),\,\ldots,\,b_q,f_q)\end{matrix}\right]$$

$$= g_1(t)$$

where

$$R(p) > 0,\ R\!\left(\sigma + \min \frac{b_j}{f_j}\right) > 0,$$

$$1 \leqslant j \leqslant m$$

$$\lambda = \sum_{j=1}^{n}\,(e_j) - \sum_{j=n+1}^{s}\,(e_j) + \sum_{j=1}^{m}\,(f_j) - \sum_{j=m+1}^{q}\,(f_j) > 0,$$

$$|\arg\,(a)\,| < \tfrac{1}{2}\,\lambda\,\pi$$

and

$$\phi_2(p) = p\ H^{\alpha,\,\beta}_{\gamma,\,\delta}\left[\,p+b\,\middle|\,\begin{matrix}(c_1,\,h_1),\,\ldots,\,(c_\gamma,\,h_\gamma)\\ (d_1,\,l_1),\,\ldots,\,(d_\delta,\,l_\delta)\end{matrix}\right]$$

$$\doteqdot \frac{e^{-bt}}{t}H^{\alpha,\,\beta}_{\gamma+1,\,\delta}\left[\frac{1}{t}\,\middle|\,\begin{matrix}(c_1,\,h_1),\,\ldots,\,(c_\gamma,\,h_\gamma),\,(0,\,1)\\ (d_1,\,l_1),\,\ldots,\,(d_\delta,\,l_\delta)\end{matrix}\right]$$

$$= g_2(t)$$

where

$$R(p) > 0,\ R(b) > 0,\ R\!\left(\frac{1-c_j}{h_j}\right) > 0,$$

$$1 \leqslant j \leqslant \beta$$

$$\sum_{j=1}^{\beta}\,(h_j) - \sum_{j=\beta+1}^{\gamma}\,(h_j) + \sum_{j=1}^{\alpha}\,(l_j) - \sum_{j=\alpha+1}^{\delta}\,(l_j) - 1 > 0$$

then putting these values in the Goldstein Theorem of Operational Calculus *viz* :

$$\int_0^\infty g_1(t)\cdot\phi_2(t)\cdot\frac{dt}{t} = \int_0^\infty g_2(t)\cdot\phi_1(t)\ \frac{dt}{t}$$

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where $\qquad \phi_r(p) \doteq g_r(t), r = 1, 2.$

we get

$$\int_0^\infty t^{\sigma-1} H_{s,\ q}^{m,\ n} \left[\alpha t \left| \begin{array}{c} (a_1\ e_1),\ \ldots,\ (a_s,\ e_s) \\ (b_1, f_1),\ \ldots,\ (b_q, f_q) \end{array} \right. \right] H_{\gamma,\ \delta}^{\alpha,\ \beta} \left[(t + b) \left| \begin{array}{c} (c_1, h_1),\ \ldots,\ (c_\gamma, h_\gamma) \\ (d_1, l_1),\ \ldots,\ (d_\delta, l_\delta) \end{array} \right. \right] dt$$

$$= \int_0^\infty e^{-bt} \cdot t^{-\sigma-1} \cdot H_{\gamma+1,\ \delta}^{\alpha,\ \beta} \left[\frac{1}{t} \left| \begin{array}{c} (c_1, h_1),\ \ldots\ldots,\ (c_\gamma, h_\gamma),\ (0, 1) \\ (d_1, l_1),\ \ldots\ldots\ (d_\delta, l_\delta) \end{array} \right. \right] \times$$

$$\times H_{s+1,\ q}^{m,\ n+1} \left[\frac{\alpha}{t} \left| \begin{array}{c} (1 - \sigma,\ 1),\ (a_1,\ e_1),\ \ldots,\ (a_s,\ e_s) \\ (b_1, f_1),\ \ldots\ldots\ldots,\ (b_q, f_q) \end{array} \right. \right] dt$$

Expanding e^{-bt} in powers of b, interchanging the order of summation and integration which is permissible vide (1; Art. 176. B), changing t to $1/t$. using (2·1) and applying (2·3) to integrate term by term we get the desired result under the conditions stated.

Putting $e_1 = 1 = \ldots = e_s = f_1 = \ldots = f_q = h_1 = \ldots = h_\gamma = l_1 = \ldots = l_\delta$ we get Saxena's result (10 ; p. 47).

But with regard to the statement of this result of Saxena attention may be invited to the following points :

(i) There appears to be a defect in the notation as r occurs in the parameters of G-function as well as in the summation.

(ii) The condition $|\arg(b)| < \pi$ is not correct. We should have $|\arg(b)| < \frac{\pi}{2}$ so that $R(b) > 0$.

(iii) Similarly in place of $\alpha + \beta > \frac{1}{2}(\gamma + \delta)$ we should have

$$\alpha + \beta > \tfrac{1}{2}(\gamma + \delta + 1)$$

Proof of (b) :

Using [2 ; p. 5(13)] and (2·2) we have

$$I = \int_0^\infty x^{\lambda-1} K_\nu(l\ x)\ K_\rho(c\ x)\ H_{p,\ q}^{m,\ n} \left[\frac{\mu}{x^\sigma} \left| \begin{array}{c} (a_1,\ e_1),\ \ldots,\ (a_p,\ e_p) \\ (b_1, f_1),\ \ldots,\ (b_q, f_q) \end{array} \right. \right] dx$$

$$= \sum_{\nu,\ -\nu} \frac{\pi}{2 \sin(-\nu\pi)} \int_0^\infty x^{\lambda-1} I_\nu(l\ x)\ K_\rho(c\ x)\ dx \times$$

$$\times \frac{1}{2\pi i} \int_L \frac{\prod\limits_{j=1}^{n} \Gamma(1 - a_j - e_j \cdot s)\ \prod\limits_{j=1}^{m} \Gamma(b_j + f_j \cdot s)}{\prod\limits_{j=n+1}^{p} \Gamma(a_j + e_j \cdot s)\ \prod\limits_{j=m+1}^{q} \Gamma(1 - b_j - f_j \cdot s)} \left(\frac{x^\sigma}{\mu} \right)^s ds$$

$$\ldots\ldots (a)$$

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In (a) changing the order of integration which may be justified as below and evaluating the x-integral with the help of [3 ; p. 334(44)] we get

$$I = \sum_{\nu, -\nu} \frac{\pi}{2 \sin(-\nu\pi)} \cdot \frac{1}{2\pi i} \int_L \frac{\prod\limits_{j=1}^{n} \Gamma(1 - a_j - e_j \cdot s) \prod\limits_{j=1}^{m} \Gamma(b_j + f_j \cdot s)}{\prod\limits_{j=n+1}^{p} \Gamma(a_j + e_j \cdot s) \prod\limits_{j=m+1}^{q} \Gamma(1 - b_j - f_j \cdot s)} \mu^{-s} \times$$

$$\times \frac{l^\nu \Gamma_*\{\tfrac{1}{2}(\lambda \pm \rho + \nu + \sigma \cdot s)\} \cdot 2^{\lambda + \sigma s - 2}}{\Gamma(\nu+1) \cdot c^{\nu + \lambda + \sigma \cdot s}} \; {}_2F_1\left[\begin{array}{c} \frac{\lambda + \rho + \nu + \sigma \cdot s}{2}, \; \frac{\lambda - \rho + \nu + \sigma \cdot s}{2} \\ \nu + 1 \end{array} ; \frac{l^2}{c^2}\right] ds$$

$$= \sum_{\nu, -\nu} \frac{\pi \cdot 2^{\lambda - 3} \cdot l^\nu}{\sin(-\nu\pi)\,\Gamma(\nu+1)\,c^{\nu+\lambda}} \cdot \times$$

$$\times \frac{1}{2\pi i} \int_L \frac{\prod\limits_{j=1}^{n} \Gamma(1 - a_j - e_j \cdot s) \prod\limits_{j=1}^{m} \Gamma(b_j + f_j \cdot s)}{\prod\limits_{j=n+1}^{p} \Gamma(a_j + e_j \cdot s) \prod\limits_{j=m+1}^{q} \Gamma(1 - b_j - f_j \cdot s)} \left\{\mu\left(\frac{c}{2}\right)^\sigma\right\}^{-s} \times$$

$$\times \Gamma_*\{\tfrac{1}{2}(\lambda \pm \rho + \nu + \sigma \cdot s)\} \sum_{r=0}^{\infty} \frac{\left(\frac{\lambda + \rho + \nu + \sigma \cdot s}{2}\right)_r \left(\frac{\lambda - \rho + \nu + \sigma \cdot s}{2}\right)_r}{\lfloor r \;\; (\nu+1)_r} \left(\frac{l}{c}\right)^{2r} ds$$

$$= \sum_{\nu, -\nu} \sum_{r=0}^{\infty} \frac{\pi \cdot 2^{\lambda - 3} \cdot l^{2r + \nu}}{\lfloor r \cdot \sin(-\nu\pi)\,\Gamma(\nu+1+r) \cdot c^{\lambda + \nu + 2r}} \times$$

$$\times \frac{1}{2\pi i} \int_L \frac{\prod\limits_{j=1}^{n} (1 - a_j - e_j \cdot s) \prod\limits_{j=1}^{m} \Gamma(b_j + f_j \cdot s)}{\prod\limits_{j=n+1}^{p} \Gamma(a_j + e_j \cdot s) \prod\limits_{j=m+1}^{q} \Gamma(1 - b_j - f_j \cdot s)} \Gamma_*\{\tfrac{1}{2}(\lambda \pm \rho + \nu + \sigma s) + r\} \left\{\mu\left(\frac{c}{2}\right)^\sigma\right\}^{-s} ds$$

$$\cdots \cdots (\beta)$$

Interpreting the integral in (β) with the help of (1·1) and (2·2), we get the desired result.

To justify the inversion of the order of integration in (a) we observe that the x-integral is absolutely convergent if

$$R\left\{\lambda \pm \nu \pm \rho + \sigma \; \frac{(1 - a_j)}{e_j}\right\} > 0, \quad |c| > |l|$$
$$1 \leqslant j \leqslant n$$

and the s-integral is absolutely convergent if

$$\gamma = \sum_{j=1}^{n}(e_j) - \sum_{j=n+1}^{p}(e_j) + \sum_{j=1}^{m}(f_j) - \sum_{j=m+1}^{q}(f_j) > 0,$$

$|\arg(\mu)| < \tfrac{1}{2}\gamma\pi.$

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The condition $|c| > |l|$ may be replaced by $R(c \pm l) > 0$ by an appeal to analytic continuation. The resulting integral in (β) is absolutely convergent under the conditions stated in (b). Therefore the inversion is justified by virtue of de la Vallee Pousin's Theorem.

Regarding the change of order of integration and summation in (β) it may be observed that the argument (l/c) of the hypergeometric function $_2F_1$ is not involved in integration and it is an analytic function of parameters under the conditions stated $(7; p. 56, Theorem 19)$.

Putting $\mu = 4$, $\sigma = 2$, $e_1 = e_2 = \ldots = e_p = f_1 = f_2 = \ldots = f_q = 1$ and changing l to p we get the result due to Sharma $(12; p. 73)$ under the relevant conditions.

Proof of (c) :

Using $(2\cdot4)$ and $(2\cdot5)$ we get

$$\sum_{\sigma, -\sigma} \frac{2^{\alpha+\beta-\frac{1}{2}} \cdot a^{\sigma} \Gamma(-\sigma)}{\gamma \cdot l^{\beta+\nu+\sigma+2/3} \cdot \Gamma(1+\nu)} \cdot \Gamma_* \{\tfrac{1}{2}(\beta + \sigma + \nu \pm \mu + 2)\} \times$$

$$\times \int_0^\infty y^{\nu-\alpha-\frac{1}{2}} \cdot H^{n+1, m+1}_{q+2, p+2}$$

$$\left[\left(\frac{1}{\lambda}\right)^{1/\lambda} \cdot \frac{2}{y} \middle|
\begin{array}{l}
\left(1-b_1, \frac{f_1}{\gamma}\right), \ldots, \left(1-b_m, \frac{f_m}{\gamma}\right), \left(\frac{1}{4} - \frac{\nu}{2} - \frac{\alpha}{2}, \frac{1}{2}\right), \\
\left(\frac{1}{4} + \frac{\nu}{2} - \frac{\alpha}{2}, \frac{1}{2}\right), \left(1-b_{m+1}, \frac{f_{m+1}}{\gamma}\right), \ldots, \left(1-b_q, \frac{f_q}{\gamma}\right) \\
\left(\frac{1+\rho+\nu}{2}, \frac{\lambda_1}{\gamma}\right), \left(1-a_1, \frac{e_1}{\gamma}\right), \ldots, \left(1-a_p, \frac{e_p}{\gamma}\right), \left(\frac{1+\rho-\nu}{2}, \frac{\lambda_2}{\gamma}\right)
\end{array}
\right]$$

$$\times F_4\left[\tfrac{1}{2}(\beta + \sigma + \nu - \mu + 2), \tfrac{1}{2}(\beta + \sigma + \nu + \mu + 2); 1 + \nu, 1 + \sigma; -\frac{y^2}{l^2}, \frac{a^2}{l^2}\right] dy$$

$$= \sqrt{l} \int_0^\infty x^{\alpha+\beta+\frac{1}{2}} K_\sigma(ax) K_\mu(lx) H^{m, n+1}_{p+2, q}\left[\frac{\lambda}{x^\gamma} \middle|
\begin{array}{l}
\left(\frac{1-\rho-\nu}{2}, \lambda_1\right), (a_1, e_1), \ldots, (a_p, e_p) \\
\left(\frac{1-\rho+\nu}{2}, \lambda_2\right) \\
(b_1, f_1), \ldots, (b_q, f_q)
\end{array}
\right] dx$$

Evaluating the integral on the right-hand side by means of (b), writing $A = \dfrac{\beta + \sigma + \nu - \mu + 2}{2}$ and $B = \dfrac{\beta + \sigma + \nu + \mu + 2}{2}$ we arrive at the desired result under the conditions stated.

Putting $\alpha + \frac{1}{2} = -\rho$, $\gamma = 2$, $\lambda = 4b^2$, $\lambda_1 = \lambda_2 = 1$, $f_1 = f_2 = \ldots = f_q = e_1 = e_2 = \ldots = e_p = 1$ we get the result due to Rathie $[8; p. 114(6)]$ under relevant conditions.

Proof of (d) :

Let

$$P = \sum_{\nu, -\nu} \sum_{r=0}^\infty \frac{\pi^{\frac{1}{2}} \operatorname{cosec}(-2\nu\pi)}{\lfloor r \Gamma(2\nu+1+r)} \times$$

$$\times H^{m+2, n}_{p, q+2}\left[z \middle|
\begin{array}{l}
(a_1, e_1), \ldots\ldots\ldots\ldots\ldots\ldots\ldots (a_p, e_p) \\
(\alpha + \nu + r, \lambda), (\beta + \nu + r, \mu), (b_1, f_1), \ldots, (b_q, f_q)
\end{array}
\right]$$

$$= R + R'$$

where from $(1\cdot1)$ we have

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$$R = \sum_{r=0}^{\infty} \frac{\pi^{\frac{1}{2}} \cosec (-2\nu\pi)}{\lfloor r \ \Gamma(2\nu+1+r)} \ H^{m+2,\ n}_{p,\ q+2} \left[z \ \Big| \ \begin{matrix} (a_1, e_1), \ldots \ldots \ldots \ldots \ldots, & (a_p, e_p) \\ (\alpha+\nu+r, \lambda), \ (\beta+\nu+r, \mu), (b_1, f_1), \ldots, (b_q, f_q) \end{matrix} \right]$$

$$= \sum_{r=0}^{\infty} \frac{\pi^{\frac{1}{2}} \cosec (-2\nu\pi)}{\lfloor r \ \Gamma(2\nu+1+r)} \times$$

$$\times \ \frac{1}{2\pi i} \int_L \frac{\prod\limits_{j=1}^{m} \Gamma(b_j - f_j.s) \ \Gamma(\alpha+\nu+r-\lambda.s) \ \Gamma(\beta+\nu+r-\mu.s) \ \prod\limits_{j=1}^{n} \Gamma(1-a_j+e_j.s). \ z^s}{\prod\limits_{j=m+1}^{q} \Gamma(1-b_j+f_j.s) \ \prod\limits_{j=n+1}^{p} \Gamma(a_j-e_j.s)} \ ds$$

$$= \frac{\pi^{\frac{1}{2}} \cosec (-2\nu\pi)}{2\pi i} \int_L \sum_{r=0}^{\infty} \frac{\Gamma(\alpha+\nu+r-\lambda.s) \ \Gamma(\beta+\nu+r-\mu.s)}{\lfloor r \ . \ \Gamma(2\nu+1+r)} \times$$

$$\times \ \frac{\prod\limits_{j=1}^{m} \Gamma(b_j - f_j.s) \ \prod\limits_{j=1}^{n} \Gamma(1-a_j+e_j.s)}{\prod\limits_{j=m+1}^{q} \Gamma(1-b_j+f_j.s) \ \prod\limits_{j=n+1}^{p} \Gamma(a_j-e_j.s)} \ .z^s. \ ds$$

$$\ldots \ldots \ldots (\gamma)$$

$$= \frac{\pi^{\frac{1}{2}} \cosec (-2\nu\pi)}{2\pi i} \int_L \frac{\prod\limits_{j=1}^{m} \Gamma(b_j - f_j.s) \ \Gamma(\alpha+\nu-\lambda.s) \ \Gamma(\beta+\nu-\mu.s) \ \prod\limits_{j=1}^{n} \Gamma(1-a_j+e_j.s)}{\Gamma(1+2\nu) \prod\limits_{j=m+1}^{q} \Gamma(1-b_j+f_j.s) \ \prod\limits_{j=n+1}^{p} \Gamma(a_j-e_j.s)} \times$$

$$\times \ {}_2F_1 \left(\begin{matrix} \alpha+\nu-\lambda s, \ \beta+\nu-\mu s \\ 2\nu+1 \end{matrix} ; 1 \right). \ z^s. \ ds$$

$$= \frac{\pi^{\frac{1}{2}} \cosec (-2\nu\pi)}{2\pi i} \int_L \frac{\prod\limits_{j=1}^{m} \Gamma(b_j - f_j.s) \ \Gamma(\alpha+\nu-\lambda.s) \ \Gamma(\beta+\nu-\mu.s) \ \prod\limits_{j=1}^{n} \Gamma(1-a_j+e_j.s)}{\prod\limits_{j=m+1}^{q} \Gamma(1-b_j+f_j.s) \ \Gamma(1+\nu-\alpha+\lambda.s) \ \Gamma(1+\nu-\beta+\mu.s)} +$$

$$\times \ \frac{\Gamma\{1-\alpha-\beta+(\lambda+\mu)s\}}{\prod\limits_{j=n+1}^{p} \Gamma(a_j-e_j.s)} \ . \ z^s. \ ds$$

(Applying Gauss's Theorem for Hypergeometric functions)

provided $R(1-\alpha-\beta+\overline{\lambda+\mu}.s) > 0$, and

$2\nu+1 \neq 0, -1, -2, -3, \ldots$.

Changing ν to $-\nu$, finding similar expression for R' and adding we get

$$P = \frac{\pi^{\frac{1}{2}}}{2\pi i} \int_L \frac{\prod\limits_{j=1}^{m} \Gamma(b_j - f_j.s) \ \prod\limits_{j=1}^{n} \Gamma(1-a_j+e_j.s) \ \Gamma(1-\alpha-\beta+\overline{\lambda+\mu}.s)}{\prod\limits_{j=m+1}^{q} \Gamma(1-b_j+f_j.s) \ \prod\limits_{j=n+1}^{p} \Gamma(a_j-e_j.s)}$$

$$\times \left\{ \sum_{\nu,\ -\nu} \frac{\cosec (-2\nu\pi) \ \Gamma(\alpha+\nu-\lambda.s) \ \Gamma(\beta+\nu-\mu.s)}{\Gamma(1+\nu-\alpha+\lambda.s) \ \Gamma(1+\nu-\beta+\mu.s)} \right\} z^s \ ds$$

[249]

Simplifying the expression in curly brackets we get

$$P = \frac{1}{\sqrt{\pi}} \cdot \frac{1}{2\pi i} \int_L \frac{\prod\limits_{j=1}^{m} \Gamma(b_j - f_j.s) \, \Gamma_*(\alpha \pm \nu - \lambda s) \, \Gamma_*(\beta \pm \nu - \mu.s) \prod\limits_{j=1}^{n} \Gamma(1 - a_j + e_j.s)}{\prod\limits_{j=m+1}^{q} \Gamma(1 - b_j + f_j.s) \prod\limits_{j=n+1}^{p} \Gamma(a_j - e_j.s) \, \Gamma(\alpha + \beta - \overline{\lambda + \mu}.s)} z^s \, ds$$

$$= \frac{1}{\sqrt{\pi}} H^{m+4,\,n}_{p+1,\,q+4} \left[z \begin{array}{l} (a_1, e_1), \, \ldots \ldots, (a_p, e_p), (\alpha + \beta, \lambda + \mu) \\ (\alpha + \nu, \lambda), (\alpha - \nu, \lambda), (\beta + \nu, \mu), (\beta - \nu, \mu), (b_1, f_1) \ldots, (b_q, f_q) \end{array} \right] \quad \ldots\ (\delta)$$

Putting $\mu = \lambda$ in (δ) using duplication formula for Gamma functions and interpreting with the help of $(1\cdot1)$ we get

$$P = 2^{1-\alpha-\beta} H^{m+4,\,n}_{p+2,\,q+4} \left[4\lambda.z \, \left| \begin{array}{l} (a_1, e_1), \, \ldots, (a_p, e_p), \left(\dfrac{\alpha+\beta}{2}, \lambda\right), \left(\dfrac{\alpha+\beta+1}{2}, \lambda\right) \\ (\alpha+\nu, \lambda), (\alpha-\nu, \lambda), (\beta+\nu, \lambda), (\beta-\nu, \lambda), (b_1, f_1), \ldots, (b_q, f_q) \end{array} \right. \right]$$

Change in the order of integration and summation in (γ) is easily seen to be justified as $\sum\limits_{r=0}^{\infty} \dfrac{(\alpha + \nu - \lambda.s)_r (\beta + \nu - \mu.s)_r}{\lfloor r \; \Gamma(1+2\nu)}$ is uniformly convergent provided $R(1 - \alpha - \beta + \overline{\lambda + \mu}.s) > 0$ and $1 + 2\nu \neq 0, -1, -2, -3, \ldots$; by virtue of $(7; p. 48 \text{ Art. } 31)$.

Putting $\lambda = 1 = e_j = f_j, j = 1, 2, 3, \ldots, p, i = 1, 2, 3, \ldots, q$, we get the result due to Sharma $(12; p. 74)$.

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Effect of Washing on some Sparingly Soluble Phosphates

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Abstract

It has been observed that the phosphates of calcium, magnesium, iron, aluminium and titanium are hydrolysed by water liberating small amounts of phosphoric acid. The results show that even the so-called sparingly soluble phosphates of iron and aluminium are also moderate suppliers of phosphate together with more soluble calcium and magnesium phosphates.

The P_2O_5 concentration in various extracts shows a gradual decrease from the first extraction to the sixth and even after the sixth extraction considerable amount of P_2O_5 goes in to the solution. The results indicate that the loss of phosphate will be much more in soils containing calcium and magnesium phosphates than in soils containing iron, aluminium and titanium phosphates.

Introduction

The solubility of various sparingly soluble phosphates in water is one of the most important factors that influence the ability to supply phosphorus to plants. Among all the phosphates present in the soil, calcium phosphate is the most important which determines the availability of the phosphate. Iron and aluminium phosphates also play a significant part in the release of phosphate in the soil solution. This release of phosphate in to the solution is believed to be brought about due to hydrolysis. Rindell (1), Cameron and Hurst (2) and Cameron and Bell (3) have shown that phosphates are hydrolysed in presence of water and the amount of phosphoric acid passing in to solution is influenced by a number of factors.

A number of workers (4–7) have reported that calcium phosphates are decomposed by water to form free phosphoric acid. Klement (8) and Cameron and Bell (9) have reported that magnesium phosphates also decompose in contact with water and liberate free phosphoric acid. Cameron and Hurst (2) observed that phosphates of iron and aluminium also hydrolyse in to phosphoric acid and their respective hydroxides. Ferrous and titanium phosphates do not hydrolyse to an appreciable extent.

Since the exact nature of the phosphates of calcium, magnesium, iron, aluminium and titanium in soils is yet unknown which are supposed to be the main suppliers of phosphate to the plants, the present study was, therefore, undertaken to investigate the washing of all these sparingly soluble phosphates.

Experimental

The phosphate samples used in these experiments were prepared in the laboratory. Analysis showed them to have a composition corresponding to the formulae, $CaHPO_4$, $CaHPO_4.2H_2O$, $Ca_3(PO_4)_2$, $MgHPO_4.3H_2O$, $Mg_3(PO_4)_2$,

$FePO_4.2H_2O$, $Fe_3(PO_4)_2.8H_2O$, $AlPO_4.H_2O$ and $Ti_3(PO_4).6H_2O$. 1 gm each of these phosphate samples was taken in a conical flask and 100 ml of distilled water added to it. The contents were shaken for 2 hours on a mechanical shaker and left to stand for 24 hours in a Thermostat maintained at a temperature of 30°C. At the end of this time, the contents were filtered. Aliquot portions of the filtrate were taken for the determination of P_2O_5, pH and electrical conductivity. The residue was transferred to the flask and the volume made up to 100 ml and similar procedure was followed as in the previous case for the subsequent washings after every 24 hours.

In the case of calcium, magnesium, ferric and aluminium phosphates, P_2O_5 was determined by precipitation method (10). Colorimetric method (11) was employed for the P_2O_5 estimation in the case of ferrous and titanium phosphates. pH of the solutions was determined by portable Cambridge pH meter and the electrical conductivity was measured by "Leitfahigkeitnsmesser" conductivity bridge (Laboratory model, S. No. 77), which is operated by mains.

Results

TABLE 1 (a)
P_2O_5 millimoles per litre

Number of the washing	$CaHPO_4$	$CaHPO_4.2H_2O$	$Ca_3(PO_4)_2$	$MgHPO_4.3H_2O$	$Mg_3(PO_4)_2$
1	0·3512	1·4387	1·0368	3·0620	1·9835
2	0·3081	1·3015	0·7479	2·0108	1·6827
3	0·2573	1·1194	0·6141	1·8742	1·3933
4	0·2447	0·9805	0·5685	1·4534	1·3080
5	0·2281	0·8473	0·5408	1·0969	1·1628
6	0·1903	0·6902	0·5310	0·8009	0·9156

TABLE 1 (b)
pH

	$CaHPO_4$	$CaHPO_4.2H_2O$	$Ca_3(PO_4)_2$	$MgHPO_4.3H_2O$	$Mg_3(PO_4)_2$
1	7·60	6·70	5·80	7·55	7·45
2	7·65	6·75	6·05	7·55	7·55
3	7·65	6·80	5·15	7·60	7·60
4	7·70	6·85	6·30	7·65	7·70
5	7·75	6·90	6·50	7·70	7·75
6	7·80	6·95	6·80	7·75	7·80

TABLE 1 (c)
Specific conductivity in mhos $\times 10^{-4}$

	$CaHPO_4$	$CaHPO_4.2H_2O$	$Ca_3(PO_4)_2$	$MgHPO_4.3H_2O$	$Mg_3(PO_4)_2$
1	1·38	3·60	2·64	5·26	3·85
2	1·67	3·12	2·19	4·53	3·36
3	1·59	2·73	1·95	4·07	2·90
4	1·50	2·40	1·86	3·62	2·50
5	1·40	2·01	1·60	3·15	2·09
6	1·28	1·59	1·37	2·40	1·72

TABLE 2 (a)

P_2O_5 millimoles per litre

Number of the washing	$FePHO_4.2H_2O$	$Fe_3(PO_4)_2.8H_2O$	$AlPO_4.H_2O$	$Ti_5(PO_4)_4.6H_2O$
1	0·3255	0·0684	0·6653	0·0102
2	0·2145	0·0628	0·4997	0·0101
3	0·1709	0·0589	0·3923	0·0100
4	0·1203	0·0581	0·3084	0·0098
5	0 0986	0·0563	0·2126	0·0097
6	0·0817	0·0559	0·1070	0·0096

TABLE 2 (b)

pH

1	6·90	6·85	7·35	6·30
2	6·90	6·85	7·45	6·30
3	6·95	6·85	7·50	6·30
4	7·00	6·90	7·55	6·30
5	7·05	6·90	7·55	6 30
6	7 15	6·95	7·65	6·35

TABLE 2 (c)

Specific conductivity in mhos $\times 10^{-4}$

1	1·08	0·36	2·18	0·04
2	0·94	0·34	1·89	0·04
3	0·82	0·33	1·61	0·04
4	0·73	0·30	1·42	·03
5	0·61	0·29	1·20	0·03
6	9·45	0·26	0·79	0 03

Discussion

From a study of the experimental results recorded in the tables 1(a) to 2(c), the effect of washing on the P_2O_5 solubility and the pH and electrical conductivity of the corresponding solutions of the phosphates of calcium, magnesium, ferrous, ferric, aluminium and titanium becomes evident. In general all these sparingly soluble phosphates are hydrolysed by water liberating small amount af phosphoric acid.

Anhydrous dicalcium phosphate has been found to be less soluble than tricalcium phosphate. whilst dihydrated dicalcium phosphate is more soluble than tricalcium phosphate. Therefore, it seems that dihydrated dicalcium phosphate is likely to be present in greater amounts, when soils are phosphated by superphosphate, finely divided rocks or basic slags. Many workers (12-14) have shown that when concentrated superphosphate or monocalcium phosphate is applied to soils, dihydrated dicalcium phosphate is one of the major products formed. But in the course of time due to the presence of fluorine in all the soils, the calcium phosphates are converted in to very sparingly soluble fluorapatites.

Like calcium, magnesium hydrophosphate – trihydrate is more soluble than tri-magnesium phosphate. Among all the phosphates studied magnesium phosphates, have been found to be most soluble and conducting in water.

Ferric and aluminium phosphates liberate much more amount of P_2O_5 in to the solution than ferrous and titanium phosphates. The amounts of P_2O_5 passing in to the solution with ferrous, ferric and titanium phosphates are less than all the calcium and magnesium phosphates and with aluminium phosphate less than all these phosphates except anhydrous dicalcium phosphate. Hence it is evident from the results that even the so-called sparingly soluble phosphates of iron, aluminium are also moderate suppliers of phosphate together with more soluble calcium and magnesium phosphates. The residual effect of phosphates reported by Scarseth and Chandler (15), Volk (16) and Ensminger and Cope (17) and the increase in the availibility of phosphate as reported by Shapiro (18), Fujiwara (19) and Mitsui (20) under flooded soils than under unflooded conditions also appears to be a consequence of hydrolysis.

It has been observed that the P_2O_5 concentration in various extracts shows a gradual decrease from the first extraction to the sixth. The electrical conductivity also likewise decreases in the various extracts which may be due to the fact that lesser number of ions are passing in to the solution. With ferrous and titanium phosphates the amount of P_2O_5 passing in to the solution changes very slightly. In the sixth extract of ferric and aluminium phosphates the amounts of P_2O_5 decrease nearly to four and six and a half times of the first extract respectively. In the cases of calcium, magnesium, ferric and aluminium phosphates, the H^+ concentration of the successive extracts decreases indicating that basic phosphates are being formed which contain more of the basic oxide than P_2O_5. With ferrous and titanium phosphates the change in pH is not significant which may be due to the fact that the P_2O_5 concentration in the various extracts does not change appreciably.

It is evident from the results that even after the sixth extraction appreciable amount of P_2O_5 goes in to the solution with calcium, magnesium, ferric and aluminium phosphates indicating that there is a great chance of the added phosphate being lost by leaching in drainage water in areas of large rainfall. The results further indicate that the loss of phosphate will be much more in soils containing calcium and magnesium phosphates than in soils containing iron, aluminium and titanium phosphates. These conclusions are in close agreement with the observations of Dhar and Misra (21) who have reported that greater amount af phosphate is leached out when the soils are richer in calcium phosphates. This washing away of phosphates from soils seems to be an important factor in causing the low recovery of phosphate by the crops.

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Infinite integrals involving products of Bessel and Meijer's G-functions*

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Abstract

Three infinite integrals involving products of Bessel and Meijer's G-functions have been evaluated in this note with the help of a theorem on Hankel transform.

1. Introduction: The well-known Hankel transform has been defined as follows :

$$(1) \qquad j_\nu \{ f(t) ; p \} = \int_0^\infty (p\,t)^{\frac{1}{2}} J_\nu(p\,t)\, f(t)\, dt, \; p > 0.$$

The object of this paper is to obtain some infinite integrals involving products of Bessel and Meijer's G-functions by utilising a theorem on Hankel transform proved in § 2. Some of the results have been expressed in terms of Appell's function F_4. A few interesting particular cases are also mentioned.

2. Theorem: If $p > 0$, $R(\alpha) > 0$, $R(\nu + 1) > 0$, $R(\nu + \xi + \frac{3}{2}) > 0$, where $f(t) = O(t^{\xi})$ for small t, $R(\eta) < 0$ where $f(t) = O(t^{\eta})$ for large t, then

$$(2) \qquad \int_0^\infty x^{\frac{1}{2}} \exp \left\{ - \frac{\alpha\, x^2}{a^2 + 16\, p^2} \right\} J_{\nu/2} \left\{ \frac{4\, p\, x^2}{a^2 + 16\, p^2} \right\} j_\nu \{ f(t) ; x \} \, dx$$

$$= \left(\frac{a^2 + 16\, p^2}{16\, p} \right)^{\frac{1}{2}} j_{\nu/2} \left\{ t^{-3/4} \exp \left(- \frac{\alpha t}{4} \right) f(t^{\frac{1}{2}}) ; p \right\}.$$

Proof: The left hand side of (2) is

$$\int_0^\infty t^{\frac{1}{2}} f(t) \left[\int_0^\infty x \exp \left\{ - \frac{\alpha\, x^2}{a^2 + 16\, p^2} \right\} J_{\nu/2} \left\{ \frac{4\, p\, x^2}{a^2 + 16\, p^2} \right\} J_\nu (t\, x) \, dx \right] dt,$$

on interchanging the order of integration. Evaluating the x-integral by [3, p. 56(2)], we get the result (2).

For the inversion of the order of integration, we must have

(i) the t-integral absolutely convergent. This is so if
$$x > 0, \; R(\nu + \xi + \tfrac{3}{2}) > 0, \; R(\eta) < 0.$$

(ii) the x-integral absolutely convergent. This is so if
$$R(\alpha) > 0, \; R(\nu + 1) > 0, \; p > 0 ; \text{ and}$$

(iii) any one of the resulting integrals absolutely convergent :
for R.H.S. to exist ; $R(\alpha) > 0, \; p > 0, \; R(\nu + \xi + \tfrac{3}{2}) > 0$.

Thus the change of the order of integration is admissible for the conditions stated with the theorem by de la Vallée Poussin theorem [2, p. 504].

3. Applications : In this section we evaluate some infinite integrals by the application of the theorem.

Example 1 : Taking

$$f(t) = t^\lambda \, \exp\left(-\frac{a^2 \, t^2}{4}\right) I_\mu\left(\frac{a^2 \, t^2}{4}\right),$$

and using [3, p. 68(8)], [1, p. 38] ; the theorem yields the following result :

$$(3) \qquad \int_0^\infty x^{-\lambda-\frac{1}{2}} \exp\left\{-\frac{a \, x^2}{a^2 + 16 \, p^2}\right\} J_{\nu/2}\left\{\frac{4 \, p \, x^2}{a^2 + 16 \, p^2}\right\}$$

$$G_{2,3}^{2,1}\left[\frac{x^2}{2 \, a^2}\,\Big|\,\begin{array}{c} 1 - \mu, \, 1 + \mu \\ \frac{3}{4} + \nu/2 + \lambda/2, \, \frac{1}{2}, \, \frac{3}{4} + \lambda/2 - \nu/2 \end{array}\right] dx$$

$$= \frac{2^{-\mu+\nu/2-1} \, p^{\nu/2} \, a^{2\mu} \, \pi^{\frac{1}{2}} \, (a^2 + 16 \, p^2)^{\frac{1}{4}} \, \Gamma\{\frac{1}{2} \, \lambda/2 + \nu/2 + \mu + \frac{3}{4}\}}{(\alpha + a^2)^{\lambda/2+\nu/2+\mu+3/4} \, \Gamma(1 + \mu) \, \Gamma(1 + \nu/2)}$$

$$F_4\left[\lambda/4 + \nu/4 + \mu/2 + \frac{3}{8}, \, \lambda/4 + \nu/4 + \mu/2 + \frac{7}{8} ; \, 1 + \nu/2, \, 1 + \mu ; \, -\frac{16p^2}{(\alpha+a^2)^2}, \, \frac{a^4}{(\alpha+a^2)^2}\right],$$

for $p > 0$, $R(\alpha) > 0$, $R(\nu + 1) > 0$, $R(\frac{3}{2} + \nu - \lambda) > 0$, $R(\lambda + \nu + 2\mu + \frac{3}{2}) > 0$.

When $\mu = 1/4 + \nu/2 - \lambda/2$, (3) gives

$$(4) \int_0^\infty x^{-\lambda/2+\nu/2-1/4} \exp\left\{-\frac{\alpha \, x^2}{a^2+16 \, p^2} - \frac{x^2}{4 \, a^2}\right\} J_{\nu/2}\left\{\frac{4p \, x^2}{a^2+16 \, p^2}\right\} W_{\frac{1}{2}(3\lambda-\nu-\frac{1}{2}), \, \frac{1}{2}(\lambda+\nu+1/2)}\left(\frac{x^2}{2a^2}\right) dx$$

$$= \frac{2^{\frac{1}{2}(3\lambda+\nu-9/2)} \, a^{\frac{1}{2}(3\nu-\lambda+3/2)} \, p^{\nu/2} \, \pi^{\frac{1}{2}} \, (a^2 + 16 \, p^2)^{\frac{1}{4}} \, \Gamma(\nu/2 + \frac{1}{2})}{\Gamma(\frac{5}{4} + \nu/2 - \lambda/2) \, \Gamma(1 + \nu/2) \, (\alpha + a^2)^{\nu+1}}$$

$$F_4\left[\nu/2 + \frac{1}{2}, \, \nu/2 + 1 ; \, \nu/2 + 1, \, \frac{5}{4} + \nu/2 - \lambda/2 ; \, -\frac{16 \, p^2}{(\alpha + a^2)^2}, \, \frac{a^4}{(\alpha + a^2)^2}\right],$$

for $\quad p > 0$, $R(\alpha) > 0$, $R(\nu + 1) > 0$, $R(a) > 0$, $R(\nu - \lambda + \frac{3}{2}) > 0$.

When $\qquad \mu = \lambda/2 + \nu/2 - 1/4$, (3) reduces to

$$(5) \qquad \int_0^\infty x^{-\lambda+\frac{1}{2}} \exp\left\{-\frac{\alpha \, x^2}{a^2 + 16 \, p^2}\right\} J_{\nu/2}\left\{\frac{4 \, p \, x^2}{a^2 + 16 \, p^2}\right\}$$

$${}_1F_1\left[1/4 + \lambda/2 + \nu/2 ; \, 3/4 - \lambda/2 + \nu/2 ; \, -\frac{x^2}{2 \, a^2}\right] dx$$

$$= \frac{2^{-\lambda/2-\frac{1}{2}} \, a^{\lambda+\nu+\frac{1}{2}} \, p^{\nu/2} \, \pi^{\frac{1}{2}} \, (a^2 + 16 \, p^2)^{\frac{1}{4}} \, \Gamma(\frac{3}{4} - \lambda/2 + \nu/2)}{(\alpha + a^2)^{\lambda+\nu+\frac{1}{2}} \, \Gamma(\frac{3}{4} + \lambda/2 + \nu/2) \, \Gamma(1 + \nu/2)}$$

$$F_4\left[\lambda/2 + \nu/2 + \frac{1}{4}, \, \lambda/2 + \nu/2 + \frac{3}{4} ; \, \nu/2 + 1, \, \frac{3}{4} + \lambda/2 + \nu/2 ; \, -\frac{16 \, p^2}{(\alpha+a^2)^2}, \, \frac{a^4}{(\alpha+a^2)^2}\right],$$

for $\quad p > 0, \quad R(\alpha) > 0, \quad R(\nu - \lambda + \tfrac{3}{2}) > 0.$

As $p \to 0$, (3) gives a known result.

Example 2. Again taking

$$f(t) = t^{2\lambda - 3/2} J_\mu (at^2),$$

and using [1, p. 38] and (2), we easily find that

(6)
$$\int_0^\infty x^{-2\lambda + 1} \exp\left\{-\frac{a\,x^2}{a^2 + 16\,p^2}\right\} J_{\nu/2}\left\{\frac{4\,p\,x^2}{a^2 + 16\,p^2}\right\}$$

$$G_{2,4}^{2,1}\left[\frac{x^4}{64\,a^2}\,\middle|\,\begin{array}{c} 1 - \mu/2,\ 1 + \mu/2 \\ \triangle(2;\lambda + \nu/2),\ \triangle(2;\lambda - \nu/2) \end{array}\right] dx$$

$$= \frac{2^{-2\lambda + \mu + \nu/2}\,a^\mu\,p^{\nu/2}\,(a^2 + 16\,p^2)^{\frac{1}{2}}\,\Gamma(\lambda + \mu + \nu/2)}{a^{\lambda + \mu + \nu/2}\,\Gamma(\nu/2 + 1)\,\Gamma(\mu + 1)}$$

$$F_4\left[\lambda/2 + \mu/2 + \nu/4,\ \lambda/2 + \mu/2 + \nu/4 + \tfrac{1}{2};\ \mu + 1,\ \nu/2 + 1;\ -\frac{16\,a^2}{a^2},\ -\frac{16\,p^2}{a^2}\right],$$

for $\quad p > 0,\ R(\alpha) > 0,\ R(\nu + 1) > 0,\ R(2\lambda + \nu + 2\mu) > 0.$

As $p \to 0$, we get a known result.

Example 3. Finally, taking

$$f(t) = t^{-3/2} \exp\left(-\frac{a}{t^2}\right),$$

and using [3, p. 30(16)], the theorem gives

(7)
$$\int_0^\infty \exp\left(-\frac{a\,x}{a^2 + 16\,p^2}\right) I_{\nu/2}\left(\frac{4\,p\,x}{a^2 + 16\,p^2}\right) G_{0,3}^{2,0}\left[\frac{a\,x}{4}\,\middle|\,\nu/2,\ 0,\ -\nu/2\right] dx$$

$$= 2(a^2 + 16\,p^2)^{\frac{1}{2}} J_{\nu/2}\left[\sqrt{\frac{a}{2}}\left\{(a^2 + 16\,p^2)^{\frac{1}{2}} - a\right\}^{\frac{1}{2}}\right] K_{\nu/2}\left[\sqrt{\frac{a}{2}}\left\{(a^2 + 16\,p^2)^{\frac{1}{2}} + a\right\}^{\frac{1}{2}}\right],$$

for $\quad R(\nu + 1) > 0,\quad R(\alpha) > 0,\quad R(a) > 0,\ p > 0.$

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On Generalised Meijer's 'H' Functions Satisfying the Truesdell F-Equations

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Abstract

In this paper several forms of the generalised Meijer's 'H' function, satisfying the Truesdell descending and ascending F–equations have been obtained. A number of results for these functions such as expansions, recurrence relations and differential properties have also been deduced with the help of the above mentioned forms.

Introduction

A theory of special functions should derive as many of the numerous formulae and properties as possible from some guiding principles. One of these principles is the F–function of Truesdell [8, p. 15].

$$\partial F(z, \alpha)/\partial z = F(z, a+1) \tag{1}$$

which is satisfied by many special functions. On the other hand the F-equation of descending type [1]

$$\partial \Upsilon(z, \alpha)/\partial z = \Upsilon(z, \alpha - 1) \tag{2}$$

is equally remarkable and is also satisfied by several special functions specially which do not satisfied the equation (1).

The object of this paper is to obtain several forms of the generalised Meijer's 'H' function, which has all the special functions as special cases, satisfying the equations (1) and (2). These forms have also been employed to deduce a number of results for this functions.

2. We define the 'H' function [5, p. 239]

$$H^{m,\,n}_{p,\,q}\left(z\,\middle|\,\begin{matrix}(a_p, e_p)\\b_q, f_q)\end{matrix}\right) = H^{m,\,n}_{p,\,q}\left(z\,\middle|\,\begin{matrix}(a_1, e_1), (a_2, e_2), \ldots, (a_p, e_p)\\(b_1, f_1), (b_2, f_2), \ldots, (b_q, f_q)\end{matrix}\right)$$

$$= \frac{1}{2\pi i}\int_L \frac{\prod\limits_{j=1}^{m}\Gamma(b_j - f_j s)\;\prod\limits_{j=1}^{n}\Gamma(1 - a_j + e_j s)}{\prod\limits_{j=m+1}^{q}\Gamma(1 - b_j + f_j s)\;\prod\limits_{j=n+1}^{q}\Gamma(a_j - e_j s)}\; z^s\, dz.$$

$$= \frac{1}{2\pi i}\int_L f(s)\, z^s\, ds \tag{3}$$

Here an empty product is interpreted as 1, $0 \leqslant m \leqslant q$, $0 \leqslant n \leqslant p$; e's and f's are all positive; L is suitable contour of Barnes type such that the poles of $\Gamma(u_j - f_j s)$, j $1, 2, \ldots, m$ lie on the right hand side of the contour and those of $\Gamma(1 - a_j + e_j s)$, j $1, 2, \ldots, n$, lie on the left hand side. Also the parameters are so restricted that the integral on the right hand side of (3) is convergent.

We shall also use the following results :

$$\Gamma(mz) = (2\pi)^{1-m/2} \, m^{mz-1/2} \, \prod_{s=1}^{m} \Gamma\left(\frac{z+(s-1)}{m}\right) \qquad (4)$$

If r is a positive integer, then with the help of (4) we get,

$$\prod_{i=0}^{m-1} \Gamma\left(\frac{r+i+\alpha}{m}\right) = m^{-r} \, (\alpha)_r \, \prod_{i=0}^{m-1} \Gamma\left(\frac{\alpha+i}{m}\right) \qquad (5)$$

and using a known result $\Gamma(1-\alpha-m)/\Gamma(1-\alpha) = (-1)^m/(\alpha)n$ $\quad a \neq$ integer, we have $\qquad (6)$

$$\prod_{i=0}^{m-1} \Gamma\left(1 - \frac{a+r+i}{m}\right) = (-1)^r \, m^r \, \prod_{i=0}^{m-1} \Gamma\left(1 - \frac{\alpha+i}{m}\right) \bigg/ (\alpha)_r \qquad (7)$$

Similarly

$$\prod_{i=0}^{m-1} \Gamma\left(\frac{\alpha-r+i}{m}\right) = (-1)^r \, m^r \, \prod_{i=0}^{m-1} \Gamma\left(\frac{a+i}{m}\right) \bigg/ (1-\alpha)_r \qquad (8)$$

and

$$\prod_{i=0}^{m-1} \Gamma\left(1 - \frac{\alpha-r+i}{m}\right) \doteq m^{-r} \, (1-\alpha)_r \, \prod_{i=0}^{m-1} \Gamma\left(1 - \frac{\alpha+i}{m}\right) \qquad (9)$$

where r/m is a positive integer.

3. Now we shall prove the following results :

$$\left(\frac{d}{dz}\right)^r H_1(z, a) = \left(\frac{d}{dz}\right)^r \left[\left(\frac{z}{\lambda}\right)^{-\alpha} H_{p, q+\lambda}^{m, n} \left(\left(\frac{z\,\xi}{\lambda}\right)^{\lambda\beta} \bigg| \begin{matrix}(a_p, e_p)\\(b_q, f_q), \triangle(\lambda, (a,\beta))\end{matrix}\right)\right]$$
$$= H_1(z, \alpha+r) \qquad (10)$$

$$\left(\frac{d}{dz}\right)^r H_2(z, a) = \left(\frac{d}{dz}\right)^r \left[\left(\frac{z}{\lambda}\right)^{-\alpha} e^{\pi i a} H_{p, q+\lambda}^{m+\lambda, n} \left(\left(\frac{z\,\xi}{\lambda}\right)^{\lambda\beta} \bigg| \begin{matrix}(a_p, e_p)\\\triangle(\lambda,(\alpha,\beta)), (b_q, f_q)\end{matrix}\right)\right]$$
$$= H_2(z, \alpha+r) \qquad (11)$$

$$\left(\frac{d}{dz}\right)^r H_3(z, a) = \left(\frac{d}{dz}\right)^r \left[\left(\frac{z}{\lambda}\right)^{\alpha-1} H_{p+\lambda, q}^{m, n} \left(\left(\frac{\xi}{\lambda z}\right)^{\lambda\beta} \bigg| \begin{matrix}(a_p, e_p), \triangle(\lambda, (\alpha, \beta))\\(b_q, f_q)\end{matrix}\right)\right]$$
$$= H_3(z, \alpha - r) \qquad (12)$$

and

$$\left(\frac{d}{dz}\right)^r H_4(z, \alpha) = \left(\frac{d}{dz}\right)^r \left[\left(\frac{z}{\lambda}\right)^{\alpha-1} e^{\pi i a} H_{p+\lambda, q}^{m, n+\lambda} \left(\left(\frac{\xi}{\lambda z}\right)^{\lambda\beta} \bigg| \begin{matrix}\triangle(\lambda, (\alpha, \beta,)), (a_p, e_p)\\(b_q, f_q)\end{matrix}\right)\right]$$
$$= H_4(z, \alpha - r) \qquad (13)$$

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where $\triangle$ $(\lambda, (a,\beta))$ denotes the parameters $\left(\dfrac{a}{\lambda}, \beta\right), \left(\dfrac{a+1}{\lambda}, \beta\right), \ldots, \left(\dfrac{a+\lambda-1}{\lambda}, \beta\right).$

Proof: To prove (10), consider

$$\left(\frac{d}{dz}\right)^r H_1(z, a) = \left(\frac{d}{dz}\right)^r \left[\left(\frac{z}{\lambda}\right)^{-a} H^{m,\,n}_{p,\,q+\lambda}\left(\left(\frac{z\xi}{\lambda}\right)^{\lambda\beta} \middle| \begin{matrix} (a_p, e_p) \\ (b_q, f_q),\ \triangle\ (\lambda,\ (a,\ \beta)) \end{matrix}\right)\right]$$

Using (3) and on interchanging the sign of differentiation and integration we get

$$\left(\frac{d}{dz}\right)^r H_1(z, a) = \frac{1}{2\,i}\int_L f(s)\ \frac{\xi^{\beta\lambda s}\ /\ \lambda^{\beta\lambda s - a}.\ \left(\dfrac{d}{dz}\right)^r [\,z^{\beta\lambda s - a}\,]}{\prod\limits_{i=0}^{\lambda-1}\Gamma\left(1 - \dfrac{a+i}{\lambda} + \beta s\right)}\ ds.$$

$$= \frac{1}{2\pi i}\left(\frac{z}{\lambda}\right)^{-(a+r)}\int_L f(s)\left(\frac{(-1)^r\ (a - \beta\lambda s)_r\ \lambda^{-r}}{\prod\limits_{i=0}^{\lambda-1}\Gamma(1 - \dfrac{a+i}{\lambda} + fs)}\right)ds.$$

Using (7) we get the required result.

Similarly the other results can be proved, on using the formulae (5) to (8). This complete the proof.

4. In this section we shall derive some results of 'H' function by applying these forms to the known theorems.

(a) By substituting the functions in (3) and (4) in the theorem [8, p. 82]

$$F(z+y, a) = \sum_{n=0}^{\infty} \frac{y^n}{n!}\ F(z, a-n)$$

we get

on replacing z by $y\,\lambda/h$ and $(y\,\xi/h)^{\lambda\beta}$ by x in succession we get,

$$\sum_{r=0}^{\infty} \frac{h^r}{r!}\ H^{m,\,n}_{p,\,q+\lambda}\left(x \middle| \begin{matrix} (a_p, e_p) \\ (b_q, f_q),\ \triangle(\lambda,\ (a - r,\ \beta)) \end{matrix}\right)$$

$$= \left(1 + \frac{n}{\lambda}\right)^{-a} H^{m,\,n}_{p,\,q+\lambda}\left(\left(1+\frac{h}{\lambda}\right)^{\beta\lambda} x \middle| \begin{matrix} (a_p, e_p) \\ (b_q, f_q),\ \triangle\ (\lambda,\ (a, \beta)) \end{matrix}\right) \quad (14)$$

and

$$\sum_{r=0}^{\infty} \frac{(-h)^r}{r!}\ H^{m+\lambda,\,n}_{p,\,q+\lambda}\left(x \middle| \begin{matrix} (a_p, e_p) \\ \triangle(\lambda,\ (a - r,\ \beta)),\ (b_q, f_q) \end{matrix}\right)$$

$$= \left(1 + \frac{h}{\lambda}\right)^{-a} H^{m+\lambda,\,n}_{p,\,q+\lambda}\left(\left(1+\frac{h}{\lambda}\right)^{\beta\lambda} x \middle| \begin{matrix} (a_p, e_p) \\ \triangle(\lambda,\ (a, \beta)),\ (b_q, f_q) \end{matrix}\right) \quad (15)$$

Similarly on substitution the functions in (12) and (13) in the theorem [1],

$$\Upsilon(z+y, a) = \sum_{j=0}^{\infty} \Upsilon^r/r!\ \Upsilon(z, a+r)$$

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and on replacing z by $y\lambda/h$ and $(h\xi/y\lambda^2)^{\lambda\beta}$ by x in succession we get,

$$\sum_{r=0}^{\infty} \frac{h^r}{r!} H^{m,\,n}_{p+\lambda,\,q} \left(x \;\middle|\; \begin{array}{c} (a_p, e_p),\ \triangle\,(\lambda,\,(\alpha+r,\,\beta)\,) \\ (b_q, f_q) \end{array} \right)$$

$$= \left(1 + \frac{h}{\lambda}\right)^{\alpha-1} H^{m,\,n}_{p+\lambda,\,q} \left(\left(1 + \frac{h}{\lambda}\right)^{-\lambda\beta} x \;\middle|\; \begin{array}{c} (a_p, e_p),\ \triangle\,(\lambda,\,(\alpha,\,\beta)\,) \\ (b_q, f_q) \end{array} \right) \quad (16)$$

and

$$\sum_{r=0}^{\infty} \frac{(-z)^r}{r!} H^{m,\,n+\lambda}_{p+\lambda,\,q} \left(x \;\middle|\; \begin{array}{c} \triangle\,(\lambda,\,(\alpha+r,\,\beta)\,),\ (a_p, e_p) \\ (b_q, f_q) \end{array} \right)$$

$$= \left(1 + \frac{h}{\lambda}\right)^{\alpha-1} H^{m,\,n+\lambda}_{p+\lambda,\,q} \left(\left(1 + \frac{h}{\lambda}\right)^{-\lambda\beta} x \;\middle|\; \begin{array}{c} \triangle\,(\lambda,(\alpha,\beta)\,),\ (a_p, e_p)) \\ (b_q, f_q) \end{array} \right)(17)$$

(b) *Derivatives* : Now put $\alpha = 0$ and replace (a_r, e_r), $r = 1, 2, \ldots, \lambda$ by $\triangle(\lambda,\,(0,\,\beta)\,)$ in (10) and (a_r, e_r), $r = p, p-1, \ldots p - \lambda + 1$ by $\triangle\,(\lambda,\,(0,\,\beta)\,)$ in (11) to obtain,

$$\left(\frac{d}{dz}\right)^r H^{m,\,n-\lambda}_{p-\lambda,\,q} \left(\left(\frac{z\xi}{\lambda}\right)^{\lambda\beta} \;\middle|\; \begin{array}{c} (a_{\lambda+1}, e_{\lambda+1}),\ \ldots,\ (a_p, e_p) \\ (b_q, f_q) \end{array} \right)$$

$$= (z/\lambda)^{-r} H^{m,\,n}_{p,\,q+\lambda} \left(\left(\frac{z\xi}{\lambda}\right)^{\lambda\beta} \;\middle|\; \begin{array}{c} \triangle\,(\lambda,\,(0,\,\beta)\,),\ (a_{\lambda+1}, e_{\lambda+1}),\ \ldots,\ (a_p, e_p) \\ (b_q, f_q),\ \triangle\,(\lambda,\,(r,\,\beta)\,) \end{array} \right)$$

and

$$\left(\frac{d}{dz}\right)^r H^{m,\,n}_{p-\lambda,\,q} \left(\frac{z\xi}{\lambda}\right)^{\lambda\beta} \;\middle|\; \begin{array}{c} (a_1, e_1),\ \ldots,\ (a_{p-\lambda}, e_{p-\lambda}) \\ (b_q, f_q) \end{array} \right)$$

$$= (-1)^r \left(\frac{z}{\lambda}\right)^{-r} H^{m+\lambda,\,n}_{p,\,q+\lambda} \left(\left(\frac{z\xi}{\lambda}\right)^{\lambda\beta} \;\middle|\; \begin{array}{c} (a_1, e_1),\ \ldots,\ (a_{p-\lambda}, e_{p-\lambda}),\ \triangle\,(\lambda,\,(0,\,\beta)\,) \\ \triangle\,(\lambda,\,(r,\,\beta)\,),\ (b_q, f_q) \end{array} \right)$$

From these results we conclude that,

$$\left(\frac{z}{\lambda}\right)^r \left(\frac{d}{dz}\right)^r H^{m,\,n}_{p,\,q} \left(\left(\frac{z\xi}{\lambda}\right)^{\lambda\beta} \;\middle|\; \begin{array}{c} (a_p, e_p) \\ (b_q, f_q) \end{array} \right)$$

$$= H^{m,\,n+\lambda}_{p+\lambda,\,q+\lambda} \left(\left(\frac{z\xi}{\lambda}\right)^{\lambda\beta} \;\middle|\; \begin{array}{c} \triangle\,(\lambda,\,(0,\,\beta)\,),\ (a_p, e_p) \\ (b_q, f_q),\ \triangle\,(\lambda,\,(r,\,\beta)\,) \end{array} \right)$$

$$= (-1)^r H^{m+\lambda,\,n}_{p+\lambda,\,q+\lambda} \left(\left(\frac{z\xi}{\lambda}\right)^{\lambda}\beta \;\middle|\; \begin{array}{c} (a_p, e_p),\ \triangle\,(\lambda,\,(0,\,\beta)\,) \\ \triangle\,(\lambda,\,(r,\,\beta)\,),\ (b_q, f_q) \end{array} \right) \quad (18)$$

Similarly from (12) and (13) we get, (on putting $\alpha = 1$).

$$\left(\frac{z}{\lambda}\right)^r \left(\frac{d}{dz}\right)^r H^{m,\,n}_{p,\,q} \left(\left(\frac{\xi}{\lambda z}\right)^{\lambda\beta} \;\middle|\; \begin{array}{c} (a_p, e_p) \\ (b_q, f_q) \end{array} \right)$$

$$= H^{m+\lambda,\,n}_{p+\lambda,\,q+\lambda} \left(\left(\frac{\xi}{\lambda z} \right)^{\lambda\beta} \Bigg| \begin{array}{l} (a_p, e_p),\, \triangle\,(\lambda,\,(1-r,\,\beta)\,) \\ \triangle\,(\lambda,\,(1,\,\beta)\,),\,(b_q, f_q) \end{array} \right)$$

$$= (-1)^r H^{m,\,n+\lambda}_{p+\lambda,\,q+\lambda} \left(\left(\frac{\xi}{\lambda z} \right)^{\lambda\beta} \Bigg| \begin{array}{l} \triangle\,(\lambda,\,(1-r,\,\beta)\,),\,(a_p, e_p) \\ (b_q, f_q),\, \triangle\,(\lambda,\,(1,\,\beta)\,) \end{array} \right) \Bigg| \quad (19)$$

(c) Recurrence Relations.

On substitution $r = 1$ in (10) and on using (18) we get,

$$\left(\frac{z}{\lambda} \right)^{-a-1} H^{m,\,n+\lambda}_{p+\lambda,\,q+2\lambda} \left(\left(\frac{z\,\xi}{\lambda} \right)^\beta \Bigg| \begin{array}{l} \triangle\,(\lambda,\,(0,\,\beta)\,),\,a_p,\,e_p) \\ (b_q, f_q),\, \triangle\,(\lambda,\,(a,\,\beta)\,),\, \triangle\,(\lambda,\,(1,\,\beta)\,) \end{array} \right)$$

$$- \frac{a}{\lambda} \left(\frac{z}{\lambda} \right)^{-a-1} H^{m,\,n}_{p,\,q+\lambda} \left(\left(\frac{z\,\xi}{\lambda} \right)^{\lambda\beta} \Bigg| \begin{array}{l} (a_p, e_p) \\ (b_q, f_q),\, \triangle\,(\lambda,\,(a,\,\beta)\,) \end{array} \right)$$

$$= \left(\frac{z}{\lambda} \right)^{-a-1} H^{m,\,n}_{p,\,q+\lambda} \left(\left(\frac{z\xi}{\lambda} \right)^{\lambda\beta} \Bigg| \begin{array}{l} (a_p, e_p) \\ (b_q, f_q),\, \triangle\,(\lambda,\,(a+1,\,\beta)\,) \end{array} \right)$$

and from (12) when $r = 1$, using (15) and (16) and on replacing a by δ, we get,

$$- \left(\frac{z}{\lambda} \right)^{\delta-2} H^{m,\,n+\lambda}_{p+2\lambda,\,q+\lambda} \left(\left(\frac{\xi}{\lambda z} \right)^{\lambda\beta} \Bigg| \begin{array}{l} \triangle(\lambda,\,(0,\,\beta)\,),\,(a_p, e_p),\, \triangle\,(\lambda,\,(\delta,\,\beta)\,) \\ (b_q, f_q),\, \triangle\,(\lambda,\,(1,\,\beta)\,) \end{array} \right)$$

$$+ \frac{\delta-1}{\lambda} \left(\frac{z}{\lambda} \right)^{\delta-2} H^{m,\,n}_{p+\lambda,\,q} \left(\left(\frac{\xi}{\lambda z} \right)^{\beta\lambda} \Bigg| \begin{array}{l} (a_p, e_p),\, \triangle\,(\lambda,\,(\delta,\,\beta)\,) \\ (bq, fq) \end{array} \right)$$

$$= \left(\frac{z}{\lambda} \right)^{\delta-2} H^{m,\,n}_{p+\lambda,\,q} \left(\left(\frac{\xi}{\lambda z} \right)^{\beta\lambda} \Bigg| \begin{array}{l} (a_p, e_p),\, \triangle\,(\lambda,\,(\delta-1,\,\beta)\,) \\ (b_q, f_q) \end{array} \right) \quad (20)$$

Now in (16), increase p by $p+\lambda$ by adding the terms $\triangle\,(\lambda,\,(\delta,\,\beta)\,)$ and replace z by x to obtain,

$$H^{m,\,n+\lambda}_{p+2\lambda,\,q+2\lambda} \left(\left(\frac{x\xi}{\lambda} \right)^{\lambda\beta} \Bigg| \begin{array}{l} \triangle\,(\lambda,\,(0,\,\beta)\,),\,(a_p, e_p),\, \triangle\,(\lambda,\,\delta,\,\beta) \\ (b_q, f_q),\, \triangle\,(\lambda,\,(a,\,\beta)\,),\, \triangle\,(\lambda,\,(1,\,\beta)\,) \end{array} \right)$$

$$= \left(\frac{a}{\lambda} \right) H^{m,\,n}_{p+\lambda,\,q+\lambda} \left(\left(\frac{x\xi}{\lambda} \right)^{\lambda\beta} \Bigg| \begin{array}{l} (a_p, e_p),\, \triangle\,(\lambda,\,(\delta,\,\beta)\,) \\ (b_q, f_q),\, \triangle\,(\lambda,\,(a,\,\beta)\,) \end{array} \right)$$

$$+ H^{m,\,n}_{p+\lambda,\,q+\lambda} \left(\left(\frac{x\xi}{\lambda} \right)^{\lambda\beta} \Bigg| \begin{array}{l} (a_p, e_p),\, \triangle\,(\lambda,\,(\delta,\,\beta)\,) \\ (b_q, f_q),\, \triangle\,(\lambda,\,(a+1,\,\beta)\,) \end{array} \right) \quad (21)$$

Similarly from (17), by increasing q by $q+\lambda$ on adding the terms $\triangle\,(\lambda,\,(a,\,\beta)\,)$ and on replacing $1/z$ by x we get,

$$H^{m,\,n+\lambda}_{p+2\lambda,\,q+2\lambda} \left(\left(\frac{x\xi}{\lambda} \right)^{\lambda\beta} \Bigg| \begin{array}{l} \triangle\,(\lambda,\,(0,\,\beta)\,),\,(a_p, e_p),\, \triangle\,(\lambda,\,\delta,\,\beta)\,) \\ (b_q, f_q),\, \triangle\,(\lambda,\,(a,\,\beta)\,),\, \triangle\,(\lambda,\,1,\,\beta)\,) \end{array} \right)$$

$$= \left(\frac{\delta-1}{\lambda} \right) H^{m,\,n}_{p+\lambda,\,q+\lambda} \left(\left(\frac{x\xi}{\lambda} \right)^{\lambda\beta} \Bigg| \begin{array}{l} (a_p, e_p),\, \triangle\,(\lambda,\,(\delta,\,\beta)\,) \\ (b_q, f_q),\, \triangle\,(\lambda,\,(a,\,\beta)\,) \end{array} \right)$$

$$- H^{m,\,n}_{p+\lambda,\,q+\lambda} \left(\left(\frac{x\xi}{\lambda} \right)^{\lambda\beta} \Bigg| \begin{array}{l} (a_p, e_p),\, \triangle\,(\lambda,\,(\delta-1,\,\beta)\,) \\ (b_q, f_q),\, \triangle\,(\lambda,\,(a,\,\beta)\,) \end{array} \right) \quad (22)$$

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On subtracting (21) from (22) we obtain

$$\left(\frac{\delta-1-\alpha}{\lambda}\right) H^{m,\,n}_{p+\lambda,\,q+\lambda}\left(z\ \middle|\ \begin{array}{l}(a_p,\,e_p),\,\triangle\,(\lambda,\,(\delta,\,\beta)\,)\\(b_q,\,f_q),\,\triangle\,(\lambda,\,(\alpha,\,\beta)\,)\end{array}\right)$$

$$=H^{m,\,n}_{p+\lambda,\,q+\lambda}\left(z\ \middle|\ \begin{array}{l}(a_p,\,e_p),\,\triangle\,(\lambda,\,(\delta,\,\beta)\,)\\(b_q,\,f_q),\,\triangle\,(\lambda,\,(\alpha+1,\,\beta))\end{array}\right)$$

$$+H^{m,\,n}_{p+\lambda,\,q+\lambda}\left(z\ \middle|\ \begin{array}{l}(a_p,\,e_p),\,\triangle\,(\lambda,\,(\delta-1,\,\beta)\,)\\(b_q,\,f_q),\,\triangle\,(\lambda,\,(\alpha,\,\beta)\,)\end{array}\right)\quad(23)$$

Similarly from (11) and (13) we get,

$$\left(\frac{1-\delta+\alpha}{\lambda}\right) H^{m+\lambda,\,n+\lambda}_{p+\lambda,\,q+\lambda}\left(z\ \middle|\ \begin{array}{l}\triangle\,(\lambda,\,(\delta,\,\beta)\,),\,(a_p,\,e_p)\\\triangle\,(\lambda,\,(\alpha,\,\beta)\,),\,(b_q,\,f_q)\end{array}\right)$$

$$=H^{m+\lambda,\,n+\lambda}_{p+\lambda,\,q+\lambda}\left(z\ \middle|\ \begin{array}{l}\triangle\,(\lambda,\,(\delta-1,\,\beta)\,),\,(a_p,\,e_p)\\\triangle\,(\lambda,\,(\alpha,\,\beta)\,),\,(b_q,\,f_q)\end{array}\right)$$

$$+H^{m+\lambda,\,n+\lambda}_{p+\lambda,\,q+\lambda}\left(z\ \middle|\ \begin{array}{l}\triangle\,(\lambda,\,(\delta,\,\beta)\,),\,(a_p,\,e_p)\\\triangle\,(\lambda,\,(\alpha+1,\,\beta)\,),\,(b_q,\,f_q)\end{array}\right)\quad(24)$$

Particular cases :

(*i*) When $e_p = f_q = \beta = 1$ for all values of p and q, then

    (*a*) all these results reduces to [2].

    (*b*) and if $\lambda = 1$ we get [4, p. 351] from (10) to (14).

    (*c*) and if $\lambda = 1$ we get [3 p. 213] from (14) to (17).

    (*d*) and if $\lambda = 1$ we get [6 p. 374] and [6, p. 486] from (18) and (19).

    (*e*) and if $\lambda = 1$ we get [3, p. 209] from (24).

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The Effects of Organic Substances on Nitrification by *Nitrobacter agilis*. Part—I

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Abstract

The effects of aldose monosaccharides on nitrification by *Nitrobacter agilis* have been studied, and it has been found that when D–glucose, D–galactose and D–mannose are present in the culture containing nitrite the rate of nitrification increases with increase in the amount of sugar upto a certain limit, above which it begins to decrease, and then at a certain point it completely stops. It has also been observed that when the bacterium is kept in contact with D-glucose, D–galactose and D–mannose alone for some time, it looses its activity the loss in activity being proportional to the amount of sugar with which the bacterium has been kept in contact, and also proportional to the time of contact with the sugar.

Introduction

Nitrification is a two step process. In the first step, ammonia is oxidised to nitrite with the help of *Nitrosomonas*, the process being called Nitrosification, and in the second step, nitrite is oxidised to nitrate by *Nitrobacter*. It is believed that nitrifying bacteria do not require organic carbon for their growth and activity. Winogradsky[1] and Waksman[2] concluded on the basis of their experiments that organic carbon is toxic for the organisms, while Muntz[3] and Beijerinck[4] showed that it is not. Tandon and Rastogi[5] have studied the effects of organic substances on *Nitrosomonas* and have found that if sugars are present in smaller amounts, they have no toxic effect on bacteria but instead serve as better food material and stimulate their growth.

In view of the conflicting results of the microbiologists on the role of organic substances on nitrification it was thought advisable to study the influence of organic substances on nitrate formers. We have carried out experiments with *Nitrobacter agilis* in the presence of different organic compounds. The results obtained with D–glucose, D–galactose and D–mannose are reported here.

Experimental

A pure culture of nitrate forming bacterium, *Nitrobacter agilis* was prepared from soil by the elective culture method employing Fred and Davenport's medium[6], the composition of which is as follows :

Sodium nitrite	1·0 g
Sodium carbonate	1·0 g
Dipotassium phosphate	0·5 g
Sodium chloride	0·5 g
Magnesium sulphate	0·3 g
Ferrous sulphate	trace
Distilled water	1000 ml.

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For the systematic study of the effects of aldoses on the process of nitrate formation, the following procedure was adopted. The following two solutions were prepared :

Solution A. Sterilized sodium nitrite containing 1 mg nitrogen perml of nitrite solution.

Solution B. Containing all the constituents of Fred and Davenport's medium except sodium nitrite.

50 ml portions of the solution B were taken in fifteen sets, each set containing twelve 250 ml conical flasks. All the flasks were sterilized.

5, 10, 20, 35, 50, 75, 100, 200, 300, 500, and 1000 mg of a sugar were added respectively to eleven flasks of each set. The twelfth flask of each set was left as such with no sugar. 0·3 ml nitrite solution was also added to each flask. One ml of a pure culture of *Nitrobacter agilis* was then added to each flask. The five sets were employed for the estimation of nitrite left, while the other five sets were employed for the estimation of total nitrite and nitrate nitrogen, and the rest five sets were used for the estimation of the sugar left. For the estimation at each time the whole contents of one requisite flask of the respective set were taken ; estimations were done after 48, 96, 168, 240, and 360 hours.

To study the effects of sugars on *Nitrobacter agilis* in the absence of nitrite, five sets of the above type containing the culture medium and the requisite amounts of the sugars were taken but no nitrite was added to them. After 48, 96, 168, 240, and 360 hours, a definite amount of inoculum from these was taken and introduced into the flask containing the culture medium along with the requisite amount of nitrite but no sugar. Nitrite was estimated in these flasks after 72 hours.

Estimation of nitrite

The amount of nitrite was estimated colorimetrically with a Photo-electric colorimeter using a mixture of 0·8 per cent solution of sulphanilic acid in acetic acid of 1·04 specific gravity and 0·5 per cent solution of α—naphthylamine in acetic acid of the same specific gravity as indicator (Griess–Ilosovay method).

Estimation of total nitrite and nitrate nitrogen

The total nitrite and nitrate nitrogen was also estimated colorimetrically with a Photo-electric colorimeter using 2% brucine solution[7] in chloroform and concentrated sulphuric acid.

Estimation of sugar

D–Glucose, D–galactose and D–mannose were estimated iodometrically[8].

TABLE 1–A

Nitrification by Nitrobacter agilis *in the presence of* D–*glucose*

(i) Volume of the medium taken = 50·0 ml

(ii) Volume of the sodium nitrite solution added = 0·3 ml

Amount of D–glucose added to the medium (in mg.)	Amount of nitrite nitrogen left at different intervals of time (in mg) Time in hours				
	48	96	168	240	360
Control	0·2880	0·1840	0·0960	0·0248	0·0000
5·00	0·2680	0·1340	0·0432	0·0092	0·0000
10·00	0·2440	0·1160	0·0304	0·0000	0·0000
20·00	0·2180	0·0981	0·0192	0·0000	0·0000
35·00	0·1900	0·0732	0·0088	0·0000	0·0000
50·00	0·1368	0·0408	0·0000	0·0000	0·0000
75·00	0·0840	0·0092	0·0000	0·0000	0·0000
100·00	0·1700	0·0568	0·0068	0·0000	0·0000
200·00	0·2520	0·1906	0·0168	0·0424	0·0000
300·00	0·2760	0·2480	0·2140	0·1640	0·1220
500·00	0·3000	0·3000	0·3000	0·3000	0·3000
1000·00	0·3000	0·3000	0·3000	0·3000	0·3000

Control = containing no D-glucose

TABLE 1–B

Nitrification by Nitrobacter agilis *which had been previously kept in contact with* D–*glucose*

(i) Volume of the culture medium taken = 50·0 ml

(ii) Volume of the Sodium nitrite solution added = 0·3 ml

Amount of D–glucose with which bacterium was kept in contact (in mg)	No of hours the bacterium had been kept in contact with D–glucose and the corresponding nitrite nitrogen in mg left after 72 hours				
	48	96	168	240	360
Control	0·0960	0·1136	0·1860	0·1920	0·2740
5·00	0·1008	0·1288	0·1940	0·2200	0·3000
10·00	0·1072	0·1420	0·1960	0·2280	0·3000
20·00	0·1340	0·1648	0·2100	0·2720	0·3000
35·00	0·1460	0·1780	0·2760	0·3000	0·3000
50·00	0·1660	0·2080	0·2740	0·3000	0·3000
75·00	0·2140	0·2380	0·3000	0·3000	0·3000
100·00	0·2240	0·3000	0·3000	0·3000	0·3000
200·00	0·2580	0·3000	0·3000	0·3000	0·3000
300·00	0·3000	0·3000	0·3000	0·3000	0·3000
500·00	0·3000	0·3000	0·3000	0·3000	0·3000
1000·00	0·3000	0·3000	0·3000	0·3000	0·3000

Control = containing no D-glucose.

TABLE 2-A

Nitrification by Nitrobacter agilis *in the presence of* D-*galactose*

(i) Volume of the culture medium taken = 50·0 ml
(ii) Volume of the sodium nitrite solution added = 0·3 ml

Amount of D-galactose added to medium (in mg)	Amount of nitrite nitrogen left at different intervals of time (in mg) Time in hours				
	48	96	168	240	360
Control	0·2920	0·1700	0·0848	0·0208	0·0000
5·0	0·2600	0·1340	0·0448	0·0068	0·0000
10·00	0·2440	0·1140	0·0208	0·0000	0·0000
20·00	0·2160	0·0928	0·0114	0·0000	0·0000
35·00	0·1920	0·0768	0·0036	0·0000	0·0000
50·00	0·1320	0·0424	0·0000	0·0000	0·0000
75·00	0·0864	0·0104	0·0000	0·0000	0·0000
100·00	0·1560	0·0648	0·0080	0·0000	0·0000
200·00	0·2080	0·1820	0·1306	0·0312	0·0000
300·00	0·2720	0·2520	0·2100	0·1860	0·1700
500·00	0·3000	0·3000	0·3000	0·3000	0·3000
1000·00	0·3000	0·3000	0·3000	0·3000	0·3000

Control = containing no D galactose.

TABLE 2-B

Nitrification by Nitrobacter agilis *which had been previously kept in contact with* D-*galactose*

(i) Volume of the culture medium taken = 50·0 ml
(ii) Volume of the sodium nitrite solution added = 0·3 ml

Amount of D-galactose with which bacterium was kept in contact (in mg)	No. of hours the bacterium had been kept in contact with D-galactose and the corresponding nitrite nitrogen left after 72 hours in mg.				
	48	96	168	240	360
Control	0·0776	0·1200	0·1872	0·1920	0·2720
5·00	0·0824	0·1292	0·1912	0·2060	0·3000
10·00	0·0928	0·1348	0·1980	0·2140	0·3000
20·00	0·1008	0·1580	0·2060	0·2680	0·3000
35·00	0·1380	0·1748	0·2620	0·3000	0·3000
50·00	0·1660	0·2060	0·3000	0·3000	0·3000
75·00	0·2120	0·2340	0·3000	0·3000	0 3000
100·00	0·2380	0·3000	0·3000	0·3000	0·3000
200·00	0·2560	0·3000	0·3000	0·3000	0·3000
300·00	0·3000	0·3000	0·3000	0·3000	0·3000
500·00	0·3000	0·3000	0·3000	0·3000	0·3000
1000·00	0·3000	0·3000	0·3000	0·3000	0·3000

Control = containing no D-galactose.

TABLE 3–A

Nitrification by Nitrobacter agilis *in the presence of* D-*mannose*

(*i*) . Volume of the culture medium taken = 50·0 ml
(*ii*) Volume of the sodium nitrite solution added = 0·3 ml

Amount of D–mannose added to the medium (in mg)	Amount of nitrite nitrogen left at different intervals of time (in mg) Time in hours				
	48	96	168	240	360
Control	0·2720	0·1700	0·0740	0·0172	0·0000
5·00	0·2520	0·1260	0·0568	0·0048	0·0000
10·00	0·2320	0·0864	0·0224	0·0000	0·0000
20·00	0·1960	0·0672	0·0136	0·0000	0·0000
35·00	0·1520	0·0328	0·0032	0·0000	0·0000
50·00	0·1248	0·0424	0·0000	0·0000	0·0000
75·00	0·0672	0·0172	0·0000	0 0000	0·0000
100·00	0·1340	0·0408	0·0000	0·0000	0·0000
200·00	0·2280	0·1560	0·0572	0·0000	0·0000
300·00	0·2840	0·2680	0·2480	0·2160	0·1760
500·00	0·3000	0·3000	0·3000	0·3000	0·3000
1000·00	0·3000	0·3000	0·3000	0·3000	0·3000

Control = containing no D–mannose.

TABLE 3–B

Nitrification by Nitrobacter agilis *which had been previously kept in contact with* D–*mannose*

(*i*) Volume of the culture medium taken = 50·0 ml
(*ii*) Volume of the sodium nitrite solution added = 0·3 ml

Amount of D–mannose with which the bacterium was kept in contact in (mg)	No. of hours the bacterium had been kept in contact with D–mannose and the corresponding nitrite nitrogen left after 70 hours				
	48	96	168	240	360
Control	0·0984	0·1280	0·1560	0·1760	0 3000
5·00	0·1168	0·1360	0·1760	0·2240	0·3000
10·00	0 1176	0·1440	0·1840	0·2280	0·3000
20·00	0·1240	0·1560	0·1960	0·2360	0·3000
35·00	0·1360	0·1640	0·2120	0·2760	0·3000
50·00	0·1440	0·1840	0·2740	0·3000	0·3000
75·00	0·1520	0·2080	3·3000	0·3000	0·3000
100·00	0·1640	0·2640	0·3000	0·3000	0·3000
200·00	0·2080	0·3000	0·3000	0·3000	0·3000
300·00	0·3000	0·3000	0·3000	0·3000	0·3000
500·00	0·3000	0·3000	0·3000	0·3000	0·3000
1000·00	0·3000	0·3000	0·3000	0·3000	0·3000

Control = containing no D–mannose.

Results and Discussion

From the Tables 1–A, 2–A and 3–A it is clear that when nitrite is present along with D–glucose, D–galactose and D–mannose repectively, there is maximum nitrite oxidation at the concentration of 75 mg sugar per 50 ml culture medium and that when the concentration of sugar goes above this, nitrite oxidation by *Nitrobacter agilis* starts decreasing.

Total nitrite and nitrate nitrogen was estimated to ascertain if there was any loss of nitrogen during the oxidation of nitrite to nitrate. It was found that the total amount of nitrit and nitrate nitrog n remained the same. From this it is concluded that all the nitrite which disappears during nitrification changes only to nitrate.

The amount of sugar left was also estimated, and it was found that in the first 48 to 96 hours a very small amount of sugar is used. It is clear from the results that the amount of sugar used up by the bacterium increases very slowly in the beginning as the nitrification increases, but after the nitrification has attained the maximum rate, the amount of sugar used begins to decrease until it stops with the cessation of nitrification.

Tables 1–B, 2–B and 3–B show, that when the bacterium is kept in contact with sugars in the absence of nitrite, its activity decreases with increase in the amount of sugar and with the number of hours it is kept in contact.

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The Effects of Organic Substances on Nitrification by *Nitrobacter agilis*. Part—II

By

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Abstract

The effects of D–arabinose, D rhamose, D–lactose, and D–maltose on nitrification by *Nitrobacter agilis* have been studied and it has been found that they are not toxic to the bacterium upto certain concentration, and that th re is no loss of nitrogen during the formation of nitrate from nitrite in their presence.

In a previous communication on the above subject (Part I),[1] our results on the effects of some aldose monosaccharides on nitrification by *Nitrobacter agilis* in pure culture were reported. In the present paper we give the results of our study on the effects of some other sugars, namely D–arabinose, D–rhamnose and D–maltose, on nitrification by *Nitrobacter agilis*.

The procedure adopted for the study was the same as already described in Part I.

TABLE 1-A

Nitrification by *Nitrobacter agilis* in the presence of D–arabinose.

(*i*) Volume of the culture medium taken = 50·0 ml.
(*ii*) Volume of the sodium nitrite solution added = 0·3 ml.

Amount of D-arabinose added to the medium (in mg)	Nitrite nitrogen left at different intervals of time (in mg.) Time in hours				
	48	96	168	240	360
Control	0·2840	0·1800	0·0968	0·0288	0·0000
5·00	0·2720	0·1288	0·0528	0·0076	0·0000
10·00	0·2380	0·1104	0·0272	0·0000	0·0000
20·00	0·1980	0·0848	0·0112	0·0000	0·0000
35·00	0·1860	0·0768	0·0104	0·0000	0·0000
50·00	0·1608	0·0552	0·0072	0·0000	0·0000
75·00	0·0872	0·0208	0·0000	0·0000	0·0000
100·00	0·1560	0·0672	0·0052	0·0000	0·0000
200·00	0·2720	0·1740	0·0982	0·0304	0·0000
300·00	0·2760	0·2520	0·2360	0·2180	0·1860
500·00	0·3000	0·3000	0·3000	0·3000	0·3000
1000·00	0·3000	0·3000	0·3000	0·3000	0·3000

Control = containing no sugar.

TABLE 2-A

Nitrification by *Nitrobacter agilis* in the presence of D–rhamnose

(*i*) Volume of the culture medium taken = 50·0 ml.
(*ii*) Volume of the sodium nitrite solution added = 0·3 ml.

Amount of D–rhamnose added to the medium (in mg)	Amount of nitrite nitrogen left at different intervals of time (in mg.) Time in hours				
	48	96	168	240	360
Control	0·2840	0·1780	0·0940	0·0328	0·0000
5·00	0·2640	0·1380	0·0528	0·0152	0·0000
10·00	0·2360	0·1088	0·0344	0·0000	0·0000
20·00	0·2180	0·0848	0·0328	0·0000	0·0000
35·00	0·1860	0·0580	0·0088	0·0000	0·0000
50·00	0·1288	0·0384	0·0000	0·0000	0·0000
75·00	0·1586	0·0962	0·0242	0·0000	0·0000
100·00	0·2040	0·1300	0·0376	0·0000	0·0000
200·00	0·2680	0·2120	0·0968	0·0248	0·0000
300·00	0·2840	0·2760	0·2520	0·2280	0·2040
500·00	0·3000	0·3000	0·3000	0·3000	0·3000
1000·00	0·3000	0·3000	0·3000	0·3000	0·3000

Control = containing no D–rhamnose.

TABLE 3-A

Nitrification by *Nitrobacter agilis* in the presence of D–lactose

(*i*) Volume of the culture medium taken = 50·0 ml.
(*ii*) Volume of the sodium nitrite solution added = 0·3 ml.

Amount of D–lactose added to the medium (in mg)	Amount of nitrite nitrogen left at different intervals of time (in mg.) Time in hours				
	48	96	168	240	360
Control	0·2760	0·1900	0·0940	0·0344	0·0000
5·00	0·2640	0·1340	0·0580	0·0092	0·0000
10·00	0·2260	0·1040	0·0340	0·0000	0·0000
20·00	0·2180	0·0900	0·0188	0·0000	0·0000
35·00	0·1680	0·0740	0·0092	0·0000	0·0000
50·00	0·1272	0·0320	0·0000	0·0000	0·0000
75·00	0·0784	0·0168	0·0000	0·0000	0·0000
100·00	0·0344	0·0000	0·0000	0·0000	0·0000
200·00	0·0840	0·0272	0·0000	0·0000	0·0000
300·00	0·1940	0·1072	0·0184	0·0000	0·0000
500·00	0·2440	0·1860	0·0860	0·0092	0·0000
1000·00	0·3000	0·3000	0·3000	0·3000	0·3000

Control = containing no D–lactose.

TABLE 4-A

Nitrification by *Nitrobacter agilis* in the presence of D-maltose

(*i*) Volume of the culture medium taken = 50·0 ml.

(*ii*) Volume of the sodium nitrite solution added = 0·3 ml.

| Amount of D-maltose added to the medium (in mg.) | Nitrite nitrogen left at different intervals of time (in mg.) | | | | |
| | Time in hours | | | | |
	48	96	168	240	360
Control	0·2760	0·1800	0·0920	0·0268	0·0000
5·00	0·2640	0·1380	0·0568	0·0172	0·0000
10·00	0·2320	0·1248	0·0384	0·0032	0·0000
20·00	0·2120	0·1100	0·0272	0·0000	0.0000
35·00	0·1780	0·0584	0·0072	0·0000	0·0000
50·00	0·1240	0·0348	0·0000	0·0000	0·0000
75·00	0·0848	0·0272	0·0000	0·0000	0·0000
100·00	0·0592	0·0064	0·0000	0·0000	0·0000
200·00	0·1280	0·0432	0·0032	0·0000	0·0000
300·00	0·2160	0·1340	0·0176	0·0068	0·0000
500·00	0·2600	0·1960	0·1380	0·0872	0·0184
1000·00	0·3000	0·3000	0·3000	0·3000	0·3000

Control = containing no D-maltose.

Results and Discussion :

Table 1–A shows that there is maximum oxidation of nitrite to nitrate at 75 mg. of arabinose, above which it decreases. Table 2–A shows that in presence of rhamnose, the maximum formation of nitrate occurs when 50 mg. of it are present. Table 3–A and 4–A show that the maximum amount of nitrate formation by *Nitrobacter agilis* in presence of lactose and maltose occurs when 100 mg. of these sugars are present; with larger amounts of sugars, the nitrate formation gradually decreases. A scrutiny of the results clearly indicates that the rate of nitrite oxidation by *Nitrobacter agilis* is accelerated by the presence of small quantities of sugars, and when the amount of sugars present is large the latter causes a depressing effect. It is also concluded from the results that the effectiveness of different sugars in stimulating the activity of nitrate forming bacterium varies from member to member, the most effective being lactose and maltose. The tolerance capacity of the bacterium for the sugars also varies with different sugars. While it can tolerate rhamnose concentration upto 50 mg./50 ml and arabinose concentration upto 75 mg./50 ml, it is able to tolerate maltose and lactose concentration upto 100 mg./50 ml.

At the beginning as well as at the end of the experiment the total nitrogen content of the respective flask was estimated and it was found that there was no loss of nitrogen.

The effect of sugars alone (in the absence of nitrite) was also studied and it was found that in the absence of nitrite in the culture medium the sugars are toxic, and that their toxicity increases with the increase in the concentration of sugars and with the number of hours the bacterium is kept in contact with the sugar.

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Bentonite as a Growth Medium for Nitrate-forming Bacteria

By

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Summary

Bentonite was used as medium of growth for nitrate-forming bacteria singly and with carbonates of calcium, magnesium and sodium, and it was found that when bentonite alone was used, the growth was very poor but when carbonates of calcium and magnesium were added to it, the growth enhanced. Calcium carbonate was found to be more effective. The presence of sodium carbonate proved injurious to the growth and activity of the bacteria.

Introduction

Clay is the most active fraction of the soil. The chemical and physical properties of the soil are dependent upon the surface activities of the clay minerals. The other two fractions of the soil, the sand and the silt, do not contribute much to the chemical properties of the soil and they are considered as skeleton of the soil. Amongst clays, silicate clays are the most widely distributed ones, although the hydrated oxide clays may also be present in tropical and subtropical soils, particularly in laterite soils. Bentonite is one of the silicate clays which may be present in the soil. The principal clay mineral content of bentonite is *montomorillonite*, although other clay minerals like *illite* and *kaolinite* and some non-clay minerals are also present.[1]

Tandon and Rastogi [2,3] have studied the growth of Nitrosomonas in bentonite medium and have found that without any optimum amount of free carbonates of calcium and magnesium, it is not a good medium for nitrite formation. The effectiveness of magnesium carbonate in stimulating the process in bentonite medium is better than that of calcium carbonate.

Since nitrate-forming bacteria also belong to the nitrifying group, we were interested in studying the nature of the growth of these bacteria also in bentonite medium. Detailed experiments were carried out for the purpose and the results obtained are discussed here.

Experimental

A pure culture of nitrate-forming bacteria was prepared from the soil by the elective culture method employing Fred and Davenport's medium[4]. This pure culture of the bacteria was employed for the proposed study.

Experiments were carried out with bentonite alone and with bentonite in combination with carbonate of calcium or magnesium or sodium.

0.2 ml sodium nitrite solution containing 0.2 mg nitrogen was taken for each experiment at the beginning, and the nitrite nitrogen left after definite intervals of time was estimated by Griess-Ilosovay method.

Discussion

From our results we find that the growth of Nitrobacter group of bacteria is very poor when only bentonite is taken as growth medium. Similar results have been obtained by Tandon and Rastogi[2,3] for Nitrosomonas group of bacteria. As the amount of bentonite in the medium is increased, the nitrite oxidation decreases (see table 1), and as the nitrite oxidation is the function of the nitrate-forming bacteria, the growth of these bacteria is also supposed to be decreased. This decrease in the growth of nitrate-forming bacteria seems to be due to the excessive swelling of bentonite as a result of the large amount of water absorbed in it due to the forces associated with the inner layer of the colloidal surface, as a consequence of which the medium becomes impervious.

TABLE 1

Nature of the medium	Nitrite nitrogen left at different intervals of time (in mg)				
	Time in hours				
	48	96	168	240	360
Fred and Davenport's medium	0·1561	0·0701	0·0058	–	–
1·0 gm bentonite	0·1779	0·1506	0·1107	0·0599	0·0174
1·5 gm bentonite	0·1851	0·1634	0·1379	0·1071	0·0675
2·0 gm bentonite	0·1888	0·1742	0·1506	0·1198	0·0762
2·5 gm bentonite	0·1924	0·1779	0·1561	0·1343	0·0951

It is also observed that when calcium carbonate is added to the bentonite medium, the rate of nitrite oxidation increases considerably, which clearly indicates that in the presence of calcium carbonate bentonite becomes more suitable for the growth and activity of the nitrate-forming bacteria. Maximum nitrate formation takes place when 0·05 gm calcium carbonate is present with 1·0 to 1·5 gm bentonite in 50 ml solution, but when higher amounts of bentonite are taken, higher amounts of calcium carbonate are also required. That is, when 2·0 to 2·5 gm bentonite is taken in the medium per 50 ml, the amount of calcium carbonate with which maximum nitrite oxidation is obtained is 0·10 gm (see table 2).

Swelling varies with the nature of adsorbed cations. The order of swelling for bentonite (Montomorillonite) is Na $\geqslant$ Li > K > Ca > Ba > H[1]. There is continuous decrease in swelling as the percentage of Ca^{++} ions in the system increases. The increase in the rate of nitrite oxidation in bentonite medium in presence of calcium carbonate may be due to this decrease in swelling.

TABLE 2

Amount of bentonite present in 50 ml solution (in gm)	Amount of CaCO₃ taken (in gm)	Nitrite nitrogen left after 168 hrs. (in mg.)
1·0	0·05	0·0167
1·5	0·05	0·0392
2·0	0·10	0·0599
2·5	0·10	0·0784

The nitrite oxidation in presence of magnesium carbonate in bentonite medium is also found to be good but it is less than that with calcium carbonate and higher than that with sodium carbonate or with no carbonate (see table 3).

This may be due to the swelling capacity of Mg^{++} ions, the swelling capacity of Mg^{++} ions being more than that of Ca^{++} and less than that of Na^+. This intermediate position of Mg^{++} may also have been due to its property of dispersion which is higher than that of Ca^{++} and lower than that of Na^+, but it is ruled out as Marshall[5] has observed that the dispersion of bentonite which is primarily composed of montomorillonite is about the same for Mg, Ca, Ba, H, Li, Na, K and NH_4 ions.

TABLE 3

Amount of bentonite present in 50 ml solution (in gm)	Amount of $MgCO_3$ taken (in gm)	Nitrite nitrogen left after 168 hours (in mg.)
1·0	0·05	0·0701
1·5	0·05	0·1107
2·0	0·10	0·1183
2·5	0·10	0·1379

The rate of nitrite oxidation in presence of sodium carbonate is very slow, even slower than that which occurs in the presence of bentonite alone. The rate of nitrate formation decreases with the increase in the amount of sodium carbonate and finally stops. Bentonite itself has a high swelling capacity and this increases with the increase in the concentration of Na^+ ions in the complex. The depressing effect of sodium carbonate might be due to this particular property of Na^+ ions in increasing the swelling of bentonite.

Thus, from the foregoing discussion it is clear that bentonite can be used satisfactorily as growth medium for Nitrobacter group of bacteria with optimum amounts of carbonates of calcium and magnesium, but this alone or with sodium carbonate is not suitable for the growth of the bacteria.

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The Effects of Organic Substances on Nitrification by
Nitrobacter agilis. Part—III

By

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Abstract

The effects of D–fructose, sucrose and raffinose on nitrification by *Nitrobacter agilis* have been studied and it has been found that like other sugars they also accelerate the rate of nitrification upto a certain limit, above which the rate decreases, and that the sugars are consumed by the bacterium in negligible amounts.

In the previous communications on the above topic (Part I and Part II)[1] the effects of glucose, galactose, mannose, arabinose, rhamnose, lactose and maltose on nitrification by *Nitrobacter agilis* have been reported. In the present paper the results of our study of the effects of D–fructose, sucrose and raffinose on nitrate formation by *Nitrobacter agilis* are given.

The process employed in the experiment and for estimation of nitrite, and of total nitrite and nitrate nitrogen was the same as described in Part I.

Estimation of Sugar

Sugars like fructose, sucrose and raffinose can not be determined by iodometric method. Therefore, these sugars were estimated by Singh and Ghosh's method[2] according to which 20 ml. N/20 copper sulphate was introduced into the flask containing the sugar. Then 10 ml of N/5 sodium hydroxide and 1·0 g sodium citrate were added. The contents were heated and acidified with N/5 acetic acid. Unreacted copper was titrated against standard sodium thiosulphate in presence of potassium iodide using starch as indicator. In the flasks containing more than 75 milligrams of sugar, larger amounts of the above reaction mixtures had to be added.

Discussion of Results

Table 1–A and 2–A show that there is maximum oxidation of nitrite to nitrate by *Nitrobacter agilis* at 100 mg of D–fructose and sucrose respectively. Table 3–A shows that with 200 mg of raffinose, there is maximum oxidation of nitrite to nitrate. Above these maximum limits of sugars, the nitrate formation by *Nitrobacter agilis* begins to decrease.

Table 1–B, 2–B and 3–B show that in the first 48 to 96 hours, a very negligible amount of sugars is consumed, and that the rate of consumption of sugars is proportional to the rate of nitrate formation. There is no more consumption of sugars after 168 hours. The exact reason for this behaviour is not very clear, but this may probably be due to some catalytic action of sugars when they come in contact with *Nitrobacter agilis* in presence of nitrite.

The effect of sugars on *Nitrobacter agilis* in the absence of nitrite has also been studied and it has been found that they are toxic when present in small amounts and that their toxicity increases with increase in their amount and with increase in the number of hours of contact with them.

TABLE 1-A

Nitrification by *Nitrobacter agilis* in the presence of D–fructose.

(*i*) Volume of the culture medium taken = 50·0 ml.
(*ii*) Volume of the sodium nitrite solution added = 0·3 ml.

Amount of D-fructose added to the medium (in mg)	Amount of nitrite nitrogen left at different intervals of time (in mg) Time in hours				
	48	96	168	240	360
Control	0·2920	0·2160	0·0860	0·0312	0·0000
5·00	0·2600	0·1640	0·0748	0·0036	0·0000
10·00	0·2320	0·1240	0·0428	0·0000	0·0000
20·00	0·2120	0·1168	0·0400	0·0000	0·0000
35·00	0·1640	0·0972	0·0198	0·0000	0·0000
50·00	0·1326	0·0254	0·0000	0·0000	0·0000
75·00	0·0840	0·0184	0·0000	0·0000	0·0000
100·00	0·0832	0·0052	0·0000	0·0000	0·0000
200·00	0·1144	0·0232	0·0000	0·0000	0·0000
300·00	0·2040	0·1352	0·0840	0·0384	0·0032
500·00	0·2680	0·2440	0·2040	0·1920	0·1800
1000·00	0·3000	0·3000	0·3000	0·3000	0·3000

Control = containing no D-fructose

TABLE 1-B

Nitrification by *Nitrobacter agilis* in the presence of D–fructose.

(*i*) Volume of the culture medium taken = 50·0 ml.
(*ii* Volume of the sodium nitrite solution added = 0·3 ml.

Amount of D-fructose added to the medium (in mg)	Amount of D–fructose left at different intervals of time (in mg.) Time in hours				
	48	96	168	240	360
Control	0·00	0·00	0·00	0·00	0·00
5·00	5·00	4·7	5·00	4·4	4·7
10·00	9·4	9·7	9·4	9·4	9·7
20·00	19·1	18·8	19·4	19·1	19·1
35·00	33·5	33·8	33·5	33·8	33·8
50·00	48·2	48·2	48·5	48·2	48·2
75·00	73·2	73·2	73·2	73·2	73·2
100·00	97 9	98·2	97·9	97·9	98·2
200 00	199·1	199·1	199·4	199·4	199·4
300·00	300·0	300·0	300·0	300·0	300·0
500·00	500·0	500·0	500·0	500·0	500·0
1000·00	1000·0	1000·0	1000·0	1000·0	1000·0

Control = containing no D-fructose

TABLE 2–A

Nitrification by *Nitrobacter agilis* in the presence of sucrose.

(*i*) Volume of the culture medium taken = 50·0 ml.

(*ii*) Volume of the sodium nitrate solution added = 0·3 ml.

Amount of sucrose added to the medium (in mg)	Nitrite nitrogen left at different intervals of time (in mg.)				
	Time in hours				
	48	96	168	240	360
Control	0·2880	0·2040	0·1112	0·0432	0·0016
5·0	0·2600	0·1560	0·0584	0·0088	0·0000
10·0	0·2160	0·1140	0·0388	0·0000	0·0000
20·0	0·1960	0·0948	0·0172	0·0000	0·0000
35·0	0·1380	0·0596	0·0052	0·0000	0·0000
50·0	0·1312	0·0408	0·0000	0·0000	0·0000
75·0	0·0792	0·0164	0·0000	0·0000	0·0000
100·0	0·0584	0·0028	0·0000	0·0000	0·0000
200·0	0·0964	0·0236	0·0036	0·0000	0·0000
300·0	0·2440	0·2160	0·1180	0·0312	0·0000
500·0	0·2680	0·2480	0·2080	0·1540	0·0840
1000·0	0·3000	0·3000	0·3000	0·3000	0·3000

Control = containing no sucrose

TABLE 2–B

Nitrification by *Nitrobacter agilis* in the presence of sucrose

(*i*) Volume of the culture medium taken = 50·0 ml

(*ii*) Volume of the sodium nitrite solution added = 0·3 ml

Amount of sucrose added to the medium (in mg)	Sucrose left at different intervals of time (in mg)				
	Time in hours				
	48	96	168	240	360
Control	0·00	0·00	0·00	0·00	0·00
5·0	5·00	5·00	4·43	4·43	4·43
10·0	10·00	10·00	9·43	9·43	9·43
20·0	19·43	18·86	18·86	18·86	18·86
35·0	33·86	33·86	32·72	32·72	32·72
50·0	48·86	47·72	47·15	47·15	47·15
75·0	71·58	71·58	71·58	71·58	71·58
100·0	97·15	97·15	97·15	97·15	97·15
200·0	198·86	198·86	197·72	197·72	197·72
300·0	298·86	299·43	300·00	300·00	300·00
500·0	500·00	500·00	500·00	500·00	500·00
1000·0	1000·00	1000·00	1000·00	1000·00	1000·00

Control = containing no sucrose.

TABLE 3–A

Nitrification by *Nitrobacter agilis* in the presence of raffinose

(i) Volume of the culture medium taken = 50·0 ml
(ii) Volume of the sodium nitrite solution added = 0·3 ml

Amount of raffinose added to the medium (in mg)	Nitrite nitrogen left at different intervals of time (in mg.) Time in hours				
	48	96	168	240	360
Control	0·2840	0·1800	0·0840	0·0172	0·0000
5·0	0·2760	0·1560	0·0352	0·0000	0·0000
10·0	0·2520	0·0984	0·0128	0·0000	0·0000
20·0	0·2200	0·0952	0·0192	0·0000	0·0000
35·0	0·1800	0·0584	0·0076	0·0000	0·0000
50·0	0·1760	0·0552	0·0052	0·0000	0·0000
75·0	0·1160	0·0072	0·0000	0·0000	0·0000
100·0	0·0840	0·0000	0·0000	0·0000	0·0000
200·0	0·0644	0·0000	0·0000	0·0000	0·0000
300·0	0·1112	0·0184	0·0000	0·0000	0·0000
500·0	0·1980	0·0852	0·0076	0·0000	0·0000
1000·0	0·3000	0·3000	0·3000	0·3000	0·3000

Control = containing no raffinose.

TABLE 3–B

Nitrification by *Nitrobacter agilis* in the presence of raffinose

(i) Volume of the culture medium taken = 50·0 ml
(ii) Volume of the sodium nitrite solution added = 0·3 ml

Amount of raffinose added to the medium (in mg)	Raffinose left at different intervals of time (in mg) Time in hours				
	48	96	168	240	360
Control	0·00	0·00	0·00	0·00	0·00
5·0	5·00	5·00	4·58	4·58	4·58
10·0	10·00	9·58	9·16	9·58	9·58
20·0	19·58	19·16	18·74	19·16	18·74
35·0	33·74	33·32	33·32	33·32	33·32
50·0	46·64	46·64	45·80	45·80	45·80
75·0	70·80	70·80	70·80	70·80	70·80
100·0	95·80	95·80	95·80	95·80	95·80
200·0	196·64	196·64	195·80	195·80	195·80
300·0	300·00	300·00	300·00	300·00	300·00
500·0	500·00	500·00	500·00	500·00	500·00
1000·0	1000·00	1000·00	1000·00	1000·00	1000·00

Control = containing no raffinose

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Coloured Chelates of the Rare Earths and their Analytical Applications, Part —I. Metal Chelates of Rare Earths with Thoron

By

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Abstract

The characteristics of the metal chelates of Thoron with Pr (III), Nd (III), Sm (III), Eu (III), Gd (III), Tb (III), Dy (III), Ho (III), Er (III), Tm (III), Yb (III) and Lu (III) have been reported. The wavelength of maximum absorption of the chelates lies at 500 mμ in each case. The metal : ligand ratio as determined by different methods is 1 : 2. The apparent stability constants of the chelates at 25° and pH 4·0 have been evaluated by three different methods and it has been observed that no particular sequence is followed in the stability of the chelates with the increase of atomic number.

In recent years renewed interest is being evinced in the chemistry of rare earths, especially on account of their similarity with the actinoids as well as in view of the growing technology of the rare earth elements.

In these laboratories a comprehensive programme of work on coloured chelates of the rare earths has been undertaken and the present series of communications record some of the work. Many of the chromogenic ligands are sensitive and compared favourably with the known chromogenic reagents for the photometric determination of the rare earth elements ; therefore, observations have also been made to study the applications of the coloured chelate formation in spectrophotometric determinations.

Kuznetsov[1] as a result of a comprehensive work on the chromogenic reactions of compounds containing an arsono group concluded that o-hydroxyazo compounds having an arsono group in ortho position to the azo group, react in an acidic medium with many elements to yield precipitates with a simultaneous change of colour. The characteristic functional groups in such compounds may be shown as

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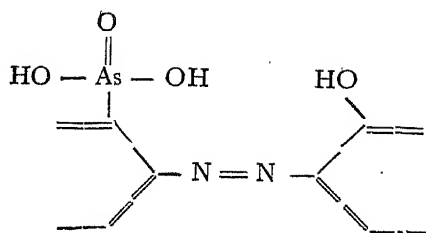
A large number of compounds of this class have been studied by Kuznetsov[t] but the most significant is 1–(o–arsonophenylazo) 2–naphthol 3 : 6 disulphonate trivially known as Thoron (abbrv. APANS). It can be represented by the following structure :
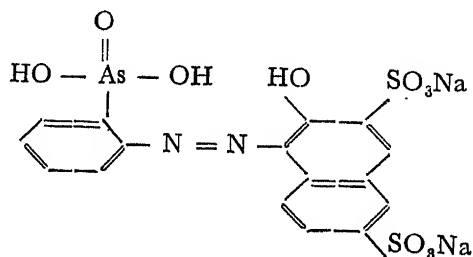
In a few publications from these laboratories the characteristics of number of APANS chelates with palladium[3], thorium[4], uranium[5], scandium[6], yttrium[7] and lanthanum[8] and their analytical applications have been reported. In continuation with the work on the metal chelates of the rare earths it has been observed that these elements form coloured chelates with APANS. In the present communication the characteristics of the rare earths-APANS chelates have been reported.

Experimental Procedure

Spectrophotometric measurements : A Unicam SP 500 spectrophotometer operated by a Doran's mains Unit on 220 V/50 cycles a.c. mains was employed for absorbance measurements. The measuring cells used were 10 mm thick.

pH measurements : pH measurements were made with Leeds and Northrup direct reading pH indicator having glass calomel electrode system supplied with the instrument.

Materials : Stock solutions of the rare earths were prepared either by dissolving the corresponding oxides (Johnson Matthey samples) in concn. hydrochloric acid or the chlorides in acidulated water containing hydrochloric acid. These solutions were standardised by the usual methods.

A stock solution of APANS was prepared by dissolving its disodium salt (B. D. H. sample) in distilled water. For all studies a freshly prepared solution of APANS was used as in the preserved solution a growth of fungus is observed.

Conditions of study : All experiments were performed at 25° ± 1° in an air-conditioned room. The pH of the solutions was adjusted to 4·0 ± 0·1 by adding snittable amount of HCl or NaOH. The chelates have a tendency to precipitate ou* therefore, 5 ml (0·5 M) solution of mannitol was added to each mixture

keeping the total volume 25 ml. The absorbance of the mixtures have been noted at 535 mμ and 545 mμ because the difference in absorbance of APANS and the chelates is considerable. To economise space only the figures of Lutecium-APANS chelate have been given as typical ones.

Results and Discussion

Nature of the complexes formed : By employing the method of Vosburgh and Cooper[9] the nature of the complexes formed was studied. For this, several mixtures containing different ratios of metal : APANS were prepared and their absorbances measured from 400 mμ to 600 mμ. At pH 4·0 the region of maximum absorption of APANS was found to be at 480 mμ, while that of rare earth chelates at 500 mμ in each case. (Fig. 1).
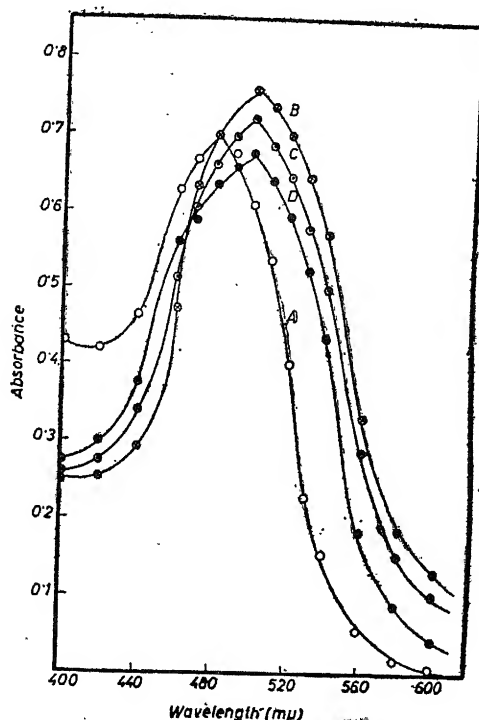
Fig. 1. Absorption spectra of lutecium–APANS chelate at pH 4·0.

Final concentration of the reactants :

Curve A   APANS = 8·0 × 10^{-5}M
Curve B   APANS = 8·0 × 10^{-5}M ;   LuCl$_3$ = 1·6 × 10^{-4}M
Curve C   APANS = 8·0 × 10^{-5}M :   LuCl$_3$ = 8·0 × 10^{-5}M
Curve D   APANS = 8·0 × 10^{-5}M ;   LuCl$_3$ = 4·0 × 10^{-5}M

Effect of pH on the stability of the chelate : Several mixtures containing rare earth metals and APANS in the ratio of 1 : 2 were prepared and adjusted to different pH values. The absorption spectra of these mixtures were recorded from 400 mμ to 600 mμ, and the λ_{max} of the mixtures were plotted. Table 1 shows the range of pH between which the various chelates are stable.

[283]
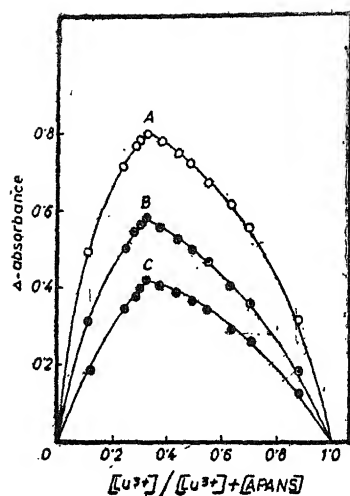
Fig. 2. Composition of lutecium–APANS chelate
at pH 4·0 and 535 mμ, using continuous
variations method $p = 1$, $p = c'/c$
Final concentration of the reactants :
Curve A   4·0 × 10⁻⁴M
Curve B   2·0 × 10⁻⁴M
Curve C   1·33 × 10⁻⁴M
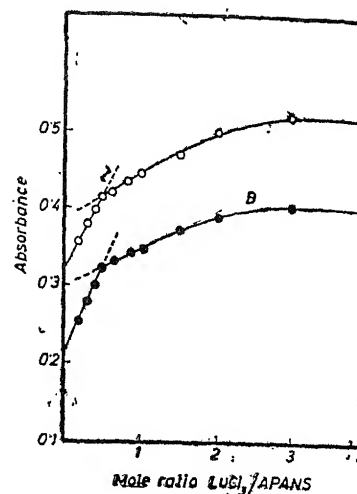
Fig. 3. Composition of lutecium–APANS
chelate by the mole ratio method
at pH 4·0 and 535 mμ.
Curve A = Final concentration of
APANS 1·0 × 10⁻⁴M
Curve B = Final concentration of
APANS 8·0 × 10⁻⁵M
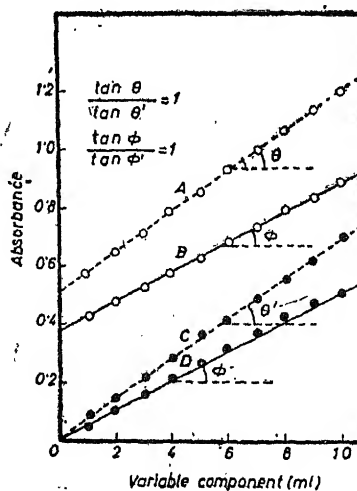
Fig. 4. Composition of lutecium–APANS chelate by the slope ratio
method at pH 4·0.

Curve A & B   APANS excess, LuCl₃ varying.
Curve C & D   LuCl₃ excess, APANS varying.
Broken line 535 mμ
Solid lines 545 mμ
10 ml (5·0 × 10⁻⁴M) excess component + x ml
(1·66 × 10⁻⁴M) variable component + 5 ml (0·5M)
mannitol + (10 − x) ml H₂O.

Composition of the chelates : The composition of the chelates have been determined spectrophotometrically using three different methods, *i.e.*, the method of continuous variations, mole ratio method and the slope ratio method. The composition has been determined at 535 mμ and 545 mμ and has been found to be 1 : 2 (Rare earth metals : APANS) (Figs. 2–4).

TABLE 1

Characteristics of rare earth chelates with APANS

pH 4·0,   Temperature 25°,   Wavelength of study 535 mμ,

Composition (Metal : APANS) 1 : 2

Chelate	pH range of stability	Average log K
Pr – (APANS)$_2$	2·5 – 8·0	9·2 $\pm$ 0·2
Nd – (APANS)$_2$	3·5 – 7·0	8·9 $\pm$ 0·2
Sm – (APANS)$_2$	2·8 – 7·6	9·6 $\pm$ 0·1
Eu – (APANS)$_2$	3·5 – 7·5	8·4 $\pm$ 0·2
Gd – (APANS)$_2$	3·5 – 8·0	8·8 $\pm$ 0·1
Tb – (APANS)$_2$	3·5 – 7·5	8·8 $\pm$ 0·1
Dy – (APANS)$_2$	3·5 – 7·5	9·3 $\pm$ 0·1
Ho – (APANS)$_2$	3·5 – 7·5	9·1 $\pm$ 0·3
Er – (APANS)$_2$	3·0 – 7·5	9·0 $\pm$ 0·2
Tm – (APANS)$_2$	3·5 – 8·0	9·4 $\pm$ 0·2
Yb – (APANS)$_2$	3·5 – 8·0	9·5 $\pm$ 0·2
Lu – (APANS)$_2$	3·5 – 8·0	9·6 $\pm$ 0·1

Evaluation of the stability constants :   In the present study stability constants determined are those obtained at a fixed temperature and pH. Attempts to maintain the ionic strength at constant level by swamping with an indifferent electrolyte could not succeed in the present work as the metal chelates precipitated by the addition of an electrolyte. For the determination of these stability constants three methods have been applied, *i.e.*, method of Dey *et al*[10], the mole ratio method[11] and the method of continuous variations[12]. The values of log K obtained in each case by different methods are in close agreement with each other. Table 1 shows the value of average log K obtained by three methods.

Suggestion on the structure of the chelates :   The lanthanoid chelates investigated in the present work have been found to be anionic in nature by electrophoresis as well as by the complete adsorption of the chelates by ion exchange resin Amberlite IR – 45 (OH). Further, on mixing the solutions of metal and the reagent, both brought individually to the same pH value, *i.e.*, 4·0, there is a drop in pH of the mixtures, showing that the hydrogen ions are liberated as a result of the chelation process. The following structure is suggested for the rare earth chelates of APANS :

[285]
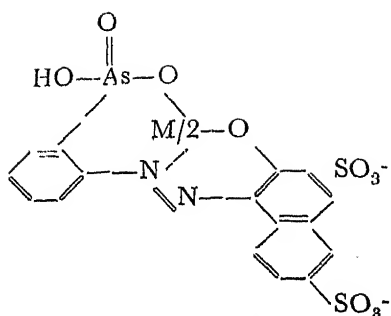
M = Rare Earth Metal

It is well known[13] that the donor properties of azo group are weak, but azo compounds which contain a strong donor group in a position ortho to the azo group form very stable chelate rings. In APANS there is a hydroxy group and an arsonic group in ortho position to the azo group, which make it suited as a chelating agent. Both these groups are capable of linking the metal ion by the removal of proton. Also the sulphonic groups are ionized at pH 4·0, as reported by Banks et al[14] and hence the above structure for the chelates seems to be justified. It should however be emphasised that the above structure is purely tentative and further information cannot be obtained from the results of the present work.

Acknowledgement

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Coloured Chelates of the Rare Earths and their Analytical Applications, Part—II. Analytical Applications of Thoron for the Determination of Rare Earths

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[Received on 19th June, 1967]

Abstract

The use of 1–(*o*–arsonophenylazo)–2–naphthol 3 : 6 disulphonate (Thoron) in the spectrophotometric determination of the rare earths have been described. Detailed conditions, *i.e.*, the characteristics of the chelates, the range of stability of the chelates with pH, adherence to Beer's Law and the sensitivity have been worked out.

In Part I of the series[1], the composition, stability and characteristics of rare earth - Thoron chelates have been described. The present paper reports the observations on analytical applications of the reagent for the spectrophotometric determination of these elements.

Experimental

Reagents and apparatus : These have already been described in Part I[1].

Conditions of study : All experiments were performed at 25°. The total volume of the mixtures prepared for measurements were 25 ml and the pH was adjusted to 4·0 by the addition of sodium hydroxide or hydrochloric acid. As the chelates have a tendency to precipitate out, therefore 5 ml (0·5 M) solution of mannitol was added in each case. Absorbance measurements were done using 10 mm thickness of solutions at 545 mμ, where the difference in absorbance between the coloured chelate and the reagent was considerable.

Results and Discussion

Characteristics of the chelates : The absorption spectra of the various chelates of APANS with rare earths show that only one complex is formed under the conditions of study. At pH 4·0, the maximum absorption of the reagent is at 480 mμ while that of all the rare earth chelates at 500 mμ. The composition of the chelates as determined by the method of continuous variations, mole ratio and the slope ratio methods is 1 : 2 (metal : ligand) in each case.

Effect of temperature on the colour intensity of the chelates : The absorbance of several mixtures containing an excess of APANS was measured at different temperatures, and it remains constant from 5° to 90°.

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Effect of pH on the stability of the chelates : Various mixtures containing metal and APANS in the ratio 1 : 2 were prepared and their absorbances measured at different wavelengths. It was observed that the range, within which a particular chelate is stable varies, as is shown in Table 1.

Confirmity to Beer's Law : The range for the adherence to Beer's law have been determined by the usual method and the results are given in the Table 1.

Sensitivity : The sensitivity indices according to the Sandell's expression are shown in Table 1.

TABLE 1

Analytical applications of APANS chelates of Rare earths

pH 4·0,　　Temperature 25°,　　Wavelength of study 545 mμ

Metal ion (III)	pH range of stability	Range for adherence to Beer's law p.p.m.	Sensitivity indices (Sandell) γ/cm^2
Pr	2·5 – 8·0	0·45 – 10·15	0·094
Nd	3·5 – 7·0	0·38 – 11·00	0·090
Sm	2·8 – 7·6	0·42 – 12·00	0·075
Eu	3·5 – 7·5	0·40 – 12·80	0·076
Gd	3·5 – 8·0	0·50 – 11·30	0·100
Tb	3·5 – 7·5	0·42 – 14·30	0·071
Dy	3·5 – 7·5	0·44 – 11·70	0·080
Ho	3·5 – 7·5	0·44 – 19·80	0·082
Er	3·0 – 7·5	0·40 – 18·60	0·063
Tm	3·5 – 8·0	0·45 – 12·10	0·084
Yb	3·5 – 8·0	0·46 – 12·40	0·086
Lu	3·5 – 8·0	0·46 – 12·50	0·087

Effect of various ions : Various ions were tested for their influence on the colour reaction and it was found that magnesium (II), calcium (II), strontium (II), barium (II), aluminium (III), tin (IV), lead (II), arsenic (III), antimony (III), bismuth (III), copper (II), silver (I), zinc (II), cadmium (II), manganese (II), cobalt (II), nickel (II), ruthenium (III), rhodium (III), sulphite, sulphate, thiosulphate, chloride, bromide, iodide and chlorate do not interfere in the determination of rare earths when APANS is used as a chromogenic reagent.

Recommended procedure : To the solution containing metal ion individually, is added a four fold excess of APANS solution and the pH adjusted to 4·0. Five ml (0·5 M) solution of mannitol is added to check precipitation of the lake. The mixture is allowed to stand for 30 minutes at 25°. The absorbance is measured at 545 mμ. The absorbance values are then compared with the calibration curve obtained under similar conditions.

Acknowledgement

Reference

1. Sangal, S. P., Sinha, S. N. and Dey, A. K. *Proc. Nat. Acad. Sci. India*, A–38, 281, 1968.

Coloured Chelates of the Rare Earths and their Analytical Applications, Part—III. Composition and Stability of the Chelates with Chrome Azurol S.

By

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[Received on 19th June, 1967]

Abstract

The composition and stability of Chrome Azurol S chelates of lanthanoids have been described. The molar ratios of the chelates as found spectrophotometrically is 1 : 1 (metal : CAS). The values of conditional stability constants (log K) of different chelates at pH 6·0 and 25° varies from 4·6 to 5·2.

Dey[1] has reviewed the applications of a number of triphenylmethane dyes. The most important ones are Aluminon, Chrome Azurol S, Xylenol Orange and Eriochrome Cyanine R. C. All these dyes have been noted to form coloured chelates with lanthanoids. Chrome Azurol S (abbrv. CAS) has been found to be very sensitive chromogenic reagent for the microdetermination of scandium, yttrium and lanthanum[2] and also for the rare earths. In the present communication the characteristics of the lanthanoid–CAS chelates have been reported.

Materials : As described earlier[3] solutions of rare earths were prepared. A stock solution of CAS (B. D. H.) was prepared in double distilled water.

Apparatus : A Unicam SP 500 spectrophotometer with 10 mm glass cells and a Leeds and Northrup direct reading pH indicator were used for absorbance and pH measurements respectively.

Conditions of study : All experiments were performed at 25°C and the pH of the solutions was 6·0 ± 0·2. The pH was adjusted by adding HCl or NaOH keeping the total volume 25 ml in each case.

Absorption spectra of the chelates : The absorption spectra of the different chelates of rare earths with CAS have been studied, which shows that the λ_{max} of CAS at pH 6·0 lies at 420 mμ while that of the chelates varies from 490 mμ to 550 mμ (Table 1) (Fig. 1).

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Stability of the chelates with pH : A number of mixtures containing (2·0×10⁻⁴M) of rare earths and CAS were prepared at different pH and their λ_{max} noted. The range of pH within which the λ_{max} of the chelate remains constant show the stability of these chelates as shown in Table 1 (Fig. 2).*

Composition of the chelate : For the determination of the molar ratio of the rare earth metals and CAS, three methods, *i.e.*, the method of continuous variations, mole ratio method and the slope ratio method were employed. Table 1 shows the composition of these chelates to be 1 : 1 (Fig. 3).
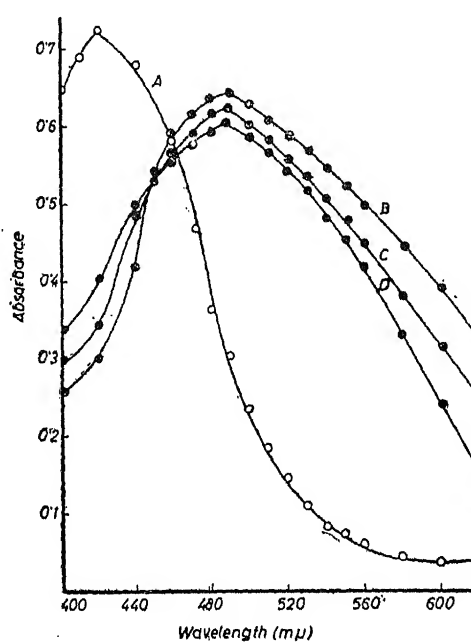
Fig. 1. Absorption spectra of Sm (III)-CAS chelate.
Final concentrations of the reactants :

Curve A. CAS = 8·0 × 10⁻⁵M.

Curve B. CAS = 8·0 × 10⁻⁵M ;
SmCl₃ 16·0 × 10⁻⁵M

Curve C. CAS = 8·0 × 10⁻⁵M ;
SmCl₃ 8·0 × 10⁻⁵M

Curve D. CAS = 8·0 × 10⁻⁵M ;
SmCl₃ 4·0 × 10⁻⁵M

Figs. with Sm only are shown here.
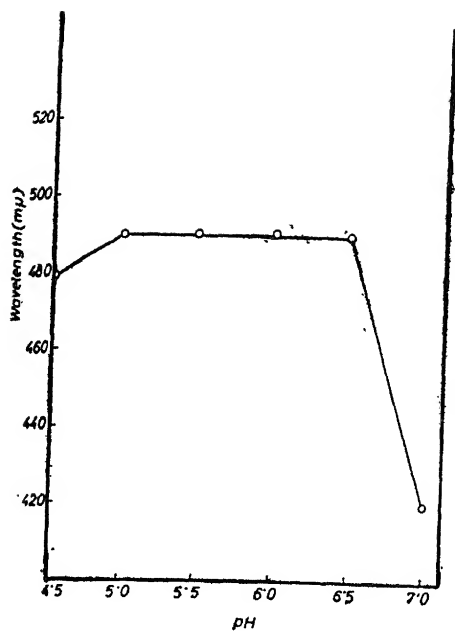
Fig. 2. Influence of pH on the stability of
the chelate.
Final concentration of the reactants :
SmCl$_3$ = 2·0 × 10^{-4}M
CAS = 2·0 × 10^{-4}M
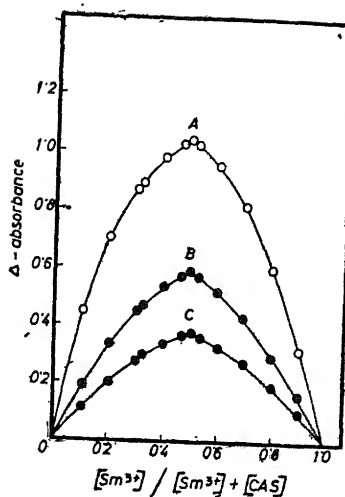
Fig. 3. Determination of the com-
position by the method of
continuous variations at
pH 6·0 and 510 mμ using
equimolar solutions.
Curve A 4·00 × 10^{-4}M
Curve B 2·00 × 10^{-4}M
Curve C 1·33 × 10^{-4}M

TABLE 1

Characteristics of lanthanoid–CAS chelates

pH 6·0 ; Temperature 25°

Metal Chelate	λ_{max} (mμ)	pH range of stability	Composition M : CAS
Ce (III) – CAS	490	5·5 – 7·5	1 : 1
Pr (III) – CAS	500	5·0 – 7·5	1 : 1
Nd (III) – CAS	490	5·5 – 6·5	1 : 1
Sm(III) – CAS	490	5·0 – 6·5	1 : 1
Eu (III) – CAS	540	4·5 – 8·5	1 : 1
Gd(III) – CAS	510	5·0 – 8·5	1 : 1
Tb (III) – CAS	500	4·5 – 8·0	1 : 1
Dy (III) – CAS	530	5·0 – 7·5	1 : 1
Ho(III) – CAS	550	5·5 – 8·5	1 : 1
Er (III) – CAS	500	5·5 – 6·5	1 : 1
Tm(III) – CAS	510	5·5 – 6·5	1 : 1
Yb (III) – CAS	550	5·5 – 8·5	1 . 1
Lu (III) – CAS	510	·5·5 – 7·0	1 : 1

[291]

Conditional stability constants : The stability constants have been determined at fixed pH 6·0 and temperature 25°C. Three different methods (*a*) method of Dey *et al*[1], (*b*) continuous variations method, and (*c*) the mole ratio method were applied for evaluating the conditional stability constants. The results obtained by all the three methods are shown in Table·2.

TABLE 2

Stability constants of lanthanoid–CAS chelates

pH 6·0 ;   Temperature 25°

Chelate of	log K by the methods employed		
	(*a*)	(*b*)	(*c*)
Ce (III)	4·5 ± 0·3	4·7 ± 0·2	4·7 ± 0·1
Pr (III)	4·8 ± 0·1	4·6 ± 0·2	4·9 ± 0·1
Nd (III)	4·5 ± 0·2	4·6 ± 0·1	4·7 ± 0·1
Sm (III)	4·8 ± 0·2	5·2 ± 0·2	5·2 ± 0·1
Eu (III)	4·2 ± 0·1	4·7 ± 0·1	4·9 ± 0·2
Gd (III)	4·4 ± 0·2	5·0 ± 0·1	5 0 ± 0·2
Tb (III)	4·7 ± 0·2	4·7 ± 0·1	4·9 ± 0·2
Dy (III)	4·2 ± 0·1	4·3 ± 0·1	4·0 ± 0·1
Ho (III)	4·3 ± 0·2	4·7 ± 0·2	4·9 ± 0·2
Er (III)	4·6 ± 0 2	4·6 ± 0·2	4·8 ± 0·1
Tm (III)	4·5 ± 0·1	4·6 ± 0·1	4·5 ± 0·1
Yb (III)	4·4 ± 0·2	4·5 ± 0·1	4·8 ± 0·1
Lu (III)	4·6 ± 0·2	4·6 ± 0·1	4·8 ± 0·1

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Colour ed Chel ates of the Rare Earths andtheir Ana ly tical Applic ations. Part—IV. Chrome Azurol S as a Sen sitive Chromogenic Reagent for the Spectrop hotometric Determination of Lanthanoids

By

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Abstract

The formation of 1 : 1 chelates of rare earths with Chrome Azurol S may be used for the spectrophotometric determination of these metals. The present studies include the absorption spectra, the effect of pH on the chelates, the range for adherence to Beer's law and sensitivity indices.

In continuation with our work on coloured chelates of the rare earths[1-3] the use of Chrome Azurol S as a sensitive reagent for the determination of these elements is being reported.

Experimental

Instruments and materials : These were the same as in Part—I[1].

Results and Discussion

Absorption spectra of the chelates :

Absorption spectra of various chelates of CAS and rare earths have been studied. It has been noted that the wavelength maxima of CAS at pH 6·0 is at 420 mμ, while the λ_{max} of different chelates varies and has been shown in Table 1.

Effect of pH on the stability of the chelates :

The range of pH within which the chelates are stable has been determined and is given in Table 1. For this, various mixtures containing individual rare earths and CAS in equimolecular ratio were prepared at different pH and their absorption spectra recorded from 400 mμ to 650 mμ. The absorption maxima of various chelates remain stable only within a definite pH range which shows the stability of the chelates.

Effect of reagent concentration :

The absorbance of solutions containing different rare earths and with varying excess of CAS were prepared at pH 6·0 and their absorbance measured at

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respective wavelengths shown in Table 1. It was found that the maximum intensity of the chelates is obtained when the reagent is present 3–4 times molar in excess.

Effect of time and temperature on the absorbance :

Mixtures of individual rare earths and CAS at pH 6·0 were found to attain the maximum absorbance value immediately but the solutions were kept for thirty minutes for attaining equilibrium. Temperature also has a negligible effect on the absorbance values. This has been confirmed by measuring the absorbance of different rare earth chelates of CAS in the 1 : 1 ratio from 10° to 90°C.

Beer's Law :

The range of concentration for the adherence to Beer's law has been determined for every rare earth metal and is shown in Table 1. For this, to 10 ml of the reagent solution varying volumes (1, 2, 3, ... 9 ml) of different rare earth metals were added and the volume was raised to 25 ml in each case. The colour intensity was measured at wavelengths shown in Table 1.

Sensitivity Indices :

The sensitivity indices of the colour reaction of different rare earth chelates as defined by Sandell, $\log I_0/I_c = 0.001$, has been determined and summarized in Table 1.

TABLE 1

Photometric determination of rare earth metals with CAS

Metal ion (III)	λ_{max} (mμ)	pH range of stability	Wavelength of study (mμ)	Range for adherence to Beer's law (p.p.m.)	Sensitivity indices (Sandell's) γ/cm^2
Ce	490	5·5 – 7·5	520	0·37 – 8·4	0·093
Pr	500	5·0 – 7·5	500	0·45 – 11·3	0·075
Nd	490	5·5 – 6·5	520	0·38 – 10·4	0·070
Sm	490	5·0 – 6·5	520	0·40 – 10·0	0·075
Eu	540	4·5 – 8·5	550	0·33 – 10·9	0·056
Gd	510	5·0 – 8·5	520	0·42 – 11·4	0·078
Tb	500	4·5 – 8·0	520	0·42 – 11·4	0·053
Dy	530	5·0 – 7·5	540	0·43 – 11·7	0·069
Ho	550	5·5 – 8·5	550	0·44 – 11·9	0·082
Er	500	5·5 – 6·5	500	0·53 – 12·0	0·167
Tm	510	5·5 – 6·5	520	0·34 – 8·1	0·113
Yb	550	5·5 – 8·5	550	0·47 – 12·5	0·113
Lu	510	5·5 – 7·0	520	0·47 – 12·6	0·140

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1. Sangal, S. P., Sinha, S. N. and Dey, A. K. *Proc. Natl. Acad. Sci., India,* A-38, 281, 1968.

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Coloured Chelates of the Rare Earths and their Analytica Applications, Part—V. Composition and Stability of the Alizarin-3-Sulphonate Chelates of Lanthanoids

By

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Abstract

The composition, stability and other characteristics of lanthanoid–ARS chelates have been described in detail. The λ_{max} of the 1 : 2 (metal : ARS) chelates lies between 520–530 mμ at pH 4·0. The chelates are stable between pH 3·0 and 7·5. The values of logarithms of stability constants determined at pH 4·0 and 25° varies between 8·3 and 9·4.

Rinehart[1] reported the use of Alizarin–3–sulphonate (Alizarin Red S ; abbr. ARS) as a sensitive chromogenic reagent for some of the rare earths. In an earlier communication we have described the coloured chelates of scandium, yttrium and lanthanum[2,3] with this ligand. In the present communication detailed studies on the composition and characteristics of the rare earth chelates of ARS have been reported.

Experimental

Instruments : A Unicam SP 500 spectrophotometer with 10 mm light path and L and N direct reading pH indicator were employed for absorption and hydrogen ion concentration measurements, respectively.

Materials : Standard solutions of ARS (B. D. H. indicator) was freshly prepared in distilled water. Stock solutions of different rare earths were prepared by dissolving the Johnson Matthey samples of oxides or chlorides in hydrochloric acid and distilled water respectively as described earlier[4].

Conditions of study : All the experiments were performed at 25° and at pH 4·0. In order to check precipitation 5 ml (0·5 M) mannitol solution was added in each case keeping the total volume 25 ml. The ionic strength of the solutions could not be adjusted because addition of the electrolyte caused the precipitation of the chelate.

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Results and Discussion

Absorption spectra of lanthanoid–ARS chelates :

Several mixtures containing $0:1$, $1:0.5$, $1:1$, and $1:2$ ratios of rare earths and ARS were prepared at pH 4·0 and their absorbances recorded from 400 mμ to 700 mμ. The absorbances were plotted against wavelength and from the curves it was concluded that the λ_{max} of ARS lies at 420 mμ while those of the rare earth chelates varied between 520 mμ and 530 mμ as shown in Table 1.

Absorption spectra of lanthanoid–ARS chelates at different pH.

Absorbance measurements of mixtures containing rare earths ($2·0 \times 10^{-4}$M) and ARS ($4·0 \times 10^{-4}$M) were carried out at different pH values. The λ_{max} of the chelates were plotted against pH and from it the range within which a particular chelate is stable was determined as shown in Table 1.

Composition of the chelates : Three different methods were used for the determination of the composition of the chelates, *i.e.*, the method of continuous variations, mole ratio method and the slope ratio method. The results of all the three methods show that the molar ratio of different chelates is $1:2$ (metal : ARS) as shown in Table 1.

TABLE 1

Characteristics of rare earth–ARS chelates

pH 4·0 ;   Temperature 25°

Chelate	λ_{max} (mμ)	pH range of stability	Composition RE (III) – ARS
Ce (III) – ARS	520	3·5 – 7·0	1 : 2
Pr (III, – ARS	520	3·5 – 7·5	1 : 2
Nd (III) – ARS	520	3·5 – 7·5	1 : 2
Sm (III) – ARS	520	3·5 – 7·0	1 : 2
Eu (III) – ARS	530	3·5 – 7·5	1 2
Gd (III) – ARS	520	4·5 – 7·5	1 : 2
Tb (III) – ARS	530	3·5 – 7·0	1 : 2
Dy (III) – ARS	525	4·0 – 7·5	1 : 2
Ho (III) – ARS	530	4·0 – 7·0	1 : 2
Er (III) – ARS	530	3·5 – 7·5	1 : 2
Tm (III) – ARS	530	3·5 – 7·5	1 : 2
Yb (III) – ARS	530	3·5 – 7·5	1 : 2
Lu (III) – ARS	530	3·5 – 7·5	1 : 2

Conditional Stability Constants

The stability constants of the chelates have been determined at fixed pH 4·0 and temperature 25°. Three different methods (*vide* Part It have been applied and the results are shown in Table 2.

TABLE 2

Stability constant (log K) of rare earth–ARS chelates

pH 4·0 ; Temperature 25°

Chelate	log K		
	Method (*a*)	Method (*b*)	Method (*c*)
Ce (III) – ARS	9·2 ± 0·3	8·8 ± 0·1	8·7 ± 0·1
Pr (III) – ARS	9·3 ± 0·2	9·1 ± 0·4	8 9 ± 0·2
Nd (III) – ARS	8·8 ± 0·3	8·4 ± 0·2	8·6 ± 0·1
Sm (III) – ARS	8·8 ± 0·2	8·4 ± 0·2	9·4 ± 0·3
Eu (III) – ARS	8·8 ± 0·3	8·5 ± 0·3	8·8 ± 0·3
Gd (III) – ARS	8·6 ± 0·4	8·6 ± 0·1	8·7 ± 0·2
Tb (III) – ARS	9·1 ± 0·4	9·0 ± 0·5	9·2 ± 0·2
Dy (III) – ARS	9·5 ± 0·2	9·4 ± 0·2	9·3 ± 0·2
Ho (III) – ARS	8·4 ± 0·4	8·7 ± 0·3	8·9 ± 0·2
Er (III – ARS	8·4 ± 0·4	8·5± 0·5	8 7 ± 0·1
Tm (III) – ARS	8·6 ± 0·2	8·3 ± 0·1	8·0 ± 0·2
Yb (III) – ARS	8·7 ± 0·5	8·6 ± 0·2	8·7 ± 0 2
Lu (III) – ARS	9·2 ± 0·4	9·2 ± 0·5	9·1 ± 0·2

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Coloured Chelates of the Rare Earths and their Analytical Applications, Part —VI. Spectrophotometric Determination of Rare Earths using Alizarin Red S as a Chromogenic Reagent

By

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Abstract

Optimum conditions for the photometric determination of rare earths using Alizarin Red S as a chromogenic reagent have been worked out. The studies include the determination of wavelength of maximum absorption, adherence to Beer's law, sensitivity indices, effect of pH on determinations and the effect of added foreign ions.

In the previous Part[1] of this series we have described the chelates of Alizarin Red S with the rare earths. The analytical applications are now being described.

Experimental

Instruments and Materials : As has been described in Part V of the series[1].

Conditions of study :

All experiments were performed at 25° keeping the pH of solutions 4·0 To check precipitation 0·5M mannitol solution (5 ml) was added in each case. The total volume was kept 25 ml.

Results and Discussion

Absorption spectra of lanthanoid—ARS chelates :

From the absorption spectra of different lanthanoid--ARS chelates (Fig. 1) it has been found that the λ_{max} of ARS at pH 4·0 lies at 420 mμ while that of the chelates of rare earths between 520 and 530 mμ (Table 1).

Effect of pH on the absorbance of the chelate :

Different solutions of rare earths and ARS in the ratio of 1 : 2 were prepared at various pH values and their absorbance spectra was recorded from 400 to 700 mμ. From the absorption spectra the absorbance of different chelates at the wavelength of study were recorded in each case. The range of pH within which the absorbance remains the same are given in Table 1.

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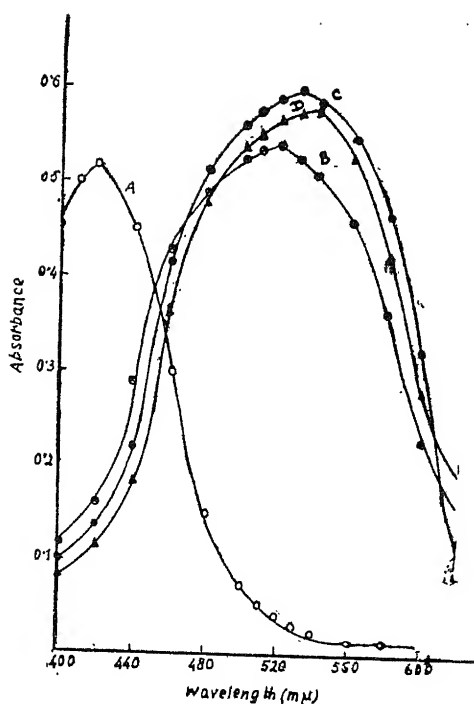
Fig. 1. Absorption spectra of lanthanoid–ARS chelates
Final concentration of the reactants.
Rare earths $= 2 \cdot 0 \times 10^{-4}$M
ARS $\quad = 4 \cdot 0 \times 10^{-4}$M

Curve A   ARS
Curve B   Ce (III), Pr (III), Nd (III), Sm (III) Gd (III), chelates.
Curve C   Dy (III) chelate
Curve D   Eu (III), Tb (III), Ho (III), Tm (III), Yb (III), Lu (III) chelates.

TABLE 1
Characteristics of lanthanoid—ARS chelates
pH $4 \cdot 0$; Temperature $25°$

Chelate	λ_{max} (mμ)	pH range of absorbance stability
Ce (III) – (ARS)$_2$	520	$4 \cdot 0 - 6 \cdot 0$
Pr (III) - (ARS)$_2$	520	$4 \cdot 0 - 5 \cdot 0$
Nd (III) – (ARS)$_2$	520	$4 \cdot 0 - 6 \cdot 0$
Sm (III) – (ARS)$_2$	520	$4 \cdot 0 - 5 \cdot 5$
Eu (III) – (ARS)$_2$	530	$4 \cdot 0 - 5 \cdot 5$
Gd (III) – (ARS)$_2$	520	$4 \cdot 0 - 5 \cdot 5$
Tb (III) – (ARS)$_2$	530	$4 \cdot 0 - 6 \cdot 0$
Dy (III) – (ARS)$_2$	525	$4 \cdot 0 - 5 \cdot 5$
Ho (III) – (ARS)$_2$	530	$4 \cdot 0 - 5 \cdot 5$
Er (III) – (ARS)$_2$	530	$4 \cdot 0 - 5 \cdot 5$
Tm (III) – (ARS)$_2$	530	$4 \cdot 0 - 6 \cdot 0$
Yb (III) – ARS)$_2$	530	$4 \cdot 0 - 6 \cdot 0$
Lu (III) – (ARS)$_2$	530	$4 \cdot 0 - 6 \cdot 0$
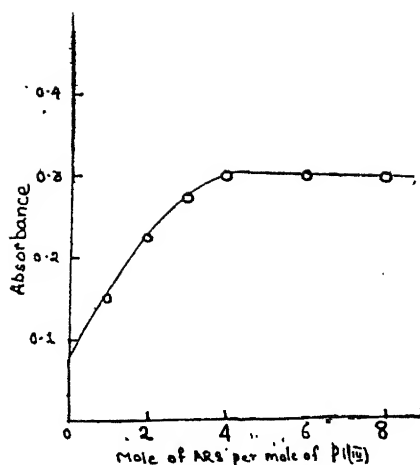
Fig. 2. Variation of colour intensity of the chelate
with increasing molar ratio of ARS at 520 mμ
Final concentration of
$PrCl_3 = 4\cdot0 \times 10^{-4}M$
$ARS = 4\cdot0 \times 10^{-3}M$
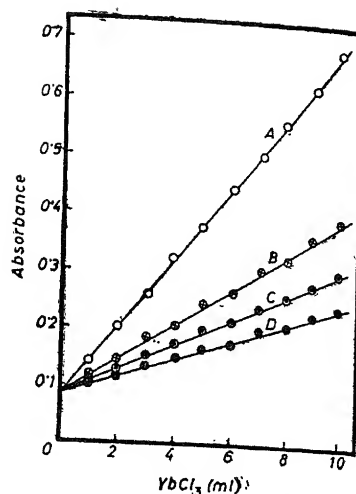
Fig. 3. Adherence to Beer's law in the
case Yb (III)–ARS system.
x ml $YbCl_3 + 5$ ml ($1\cdot0 \times 10^{-3}M$)
ARS + 5 ml ($0\cdot5M$) mannitol +
$(15 - x)$ ml H_2O.
Curve A – $2\cdot00 \times 10^{-4}M$ $YbCl_3$
Curve B – $1\cdot00 \times 10^{-4}M$ $YbCl_3$
Curve C – $8\cdot00 \times 10^{-5}M$ $YbCl_3$
Curve D – $6\cdot67 \times 10^{-5}M$ $YbCl_3$

Effect of time and temperature on the colour intensity :

Solutions containing $2\cdot0 \times 10^{-4}M$ rare earths and $4\cdot0 \times 10^{-4}M$ ARS were prepared at pH 4·0. Their absorbances were noted at 530 mμ at room temperature and after an interval of 1, 2, 4 and 8 hours. It was observed that the colour intensity of the chelates remain constant upto 2 hours, although after that the precipitation takes place. The effect of temperature on the colour intensity has also been studied, and it has been noted that at lower temperature there is no appreciable change in colour intensity but at higher temperature the precipitation of the lake takes place.

Effect of ARS concentration on the colour intensity

Different solutions containing various rare earths were prepared at pH 4·0. ARS was then added in different amounts from 1, 2, 3, 4, 5, 6, 7 and 8 fold in excess. The absorbance of these solutions were measured at 530 mμ and it was found that the maximum intensity of the colour is obtained when ARS is present four fold excess (Fig. 2).

Effect of added foreign ions

Different solutions containing $(2\cdot0 \times 10^{-4}M)$ rare earths and $(4\cdot0 \times 10^{-4}M)$ ARS were prepared at pH 4·0 and their absorbance was measured in the presence of different concentration of various cations and anions. It was observed that cations such as Cu (II), Fe (III), Fe (II), Al (III), Be (II), Th (IV), Ce (III), Mo (V), UO_2 (II), Ti (IV), In (III), Pd (II), Sc (III), Y (III), La (III), and anions as citrate, tartarate, borate and oxalate interfered at all concentrations.

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Hence for the determination of individual rare earths the elimination of these ions, if present, is necessary.

Adherence to Beer's Law

The range of concentration within which the Beer's law is valid has been determined for various rare earths and the results are shown in Fig. 3 and Table 2.

Sensitivity Indices : The sensitivity indices of the reactions between rare earths and ARS were determined and the values are given in Table 2.

TABLE 2

Analytical application of ARS in the determination of lanthanoids

pH 4·0 ;   Wavelength of study 530 mμ

Metal ion (III)	Range for adherence to Beer's law p.p.m.	Range for effective photometric determination p.p.m.	Sensitivity Index (Sandell) γ/cm^2
Ce	0·45 − 10·0	0·60 − 8·0	0·093
Pr	0·45 − 10·0	0·60 − 8·0	0·090
Nd	0·46 − 10·4	0·60 − 8·0	0·072
Sm	0·48 − 10·4	0·65 − 8·0	0·100
Eu	0·48 − 10·9	0·65 − 8·5	0·100
Gd	0·42 − 12·8	0 60 − 11·0	0·078
Tb	0·42 − 12·9	0·60 − 11·0	0·070
Dy	0·44 − 11·7	0·60 − 10·0	0·080
Ho	0·45 − 20·0	0·60 − 16·0	0·082
Er	0·40 − 18·6	0·60 − 14·5	0·083
Tm	0·45 − 12·1	0·65 − 10·0	0·084
Yb	0·46 − 13·9	0·60 − 11·0	0·086
Lu	0·46 − 14·0	0·60 − 12·0	0·086

Recommended Procedure :   A mixture containing the individual rare earths and ARS (four fold molar excess) is prepared at pH 4·0.   5 ml (0·5M) mannitol solution is added and then the volume is raised to 25 ml.   The absorbance of the mixture is now recorded at 530 mμ and by comparision with the standard curve obtained under identical conditions the concentration of unknown solution can be found.

Acknowledgement

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Coloured Chelates of Rare Earths and their Analytical Applications, Part—VII. Composition and Stability of Lanthanoid-Chromotrope 2B Chelates

By

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Abstracts

The formation of pink coloured chelates of lanthanoids with CTB having λ_{max} between 530 mμ and 545 mμ have been studied. The composition of the chelates is 1:1 (metal : CTB) in each case. Stability constants of the chelates at pH 6·0 and 25° have also been evaluated by three different methods.

p-Nitrobenzene azochromotropic acid trivially known as Chromotrope 2B (abbrv. CTB) may be represented by the following structure :
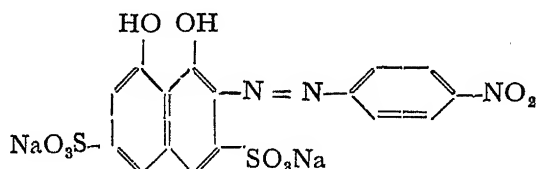
The reagent has attracted some attention from the viewpoint of its chromogenic behaviour. Dey and coworkers observed that CTB form pink coloured chelates with scandium, yttrium and lanthanum and the rare earths. In view of the interesting chromogenic reactions of the reagent Munshi and Dey[1] carried out a detailed study of CTB chelates of scandium and yttrium, while Sangal, Srivastava and Dey[2] reported the characteristics of the lanthanum chelate. Sangal further reported the use of this reagent in the photometric determination of scandium, yttrium and lanthanum[3,4]. As has been said earlier that rare earths also give a pink coloured chelate with CTB, therefore, Dey and coworkers undertook a comprehensive study of the rare earth chelates with CTB and have reported the analytical applications of the reagent in the microdetermination of the metals[5]. In the present paper the results on the composition, stability and other characteristics of the lanthanoids–CTB chelates have been communicated.

Experimental

Materials : The chlorides of the rare earth solutions were prepared as described earlier[6]. A stock solution of Chromotrope 2B (disodium salt) was

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prepared by dissolving a requisite amount of the compound in distilled water and then diluted suitably to obtain solutions of various concentrations.

Apparatus : A Leeds and Northrup direct reading pH indicator and a Unicam SP 500 spectrophotometer as described earlier[6].

Conditions of study : Experiments were done at 25° and pH 6·0 keeping the total volume 25 ml in each case. It may be mentioned that in view of the high value of absorbance of CTB at the λ_{max} of the chelates, it was desirable to make the observations at a wavelength more towards the red region of the spectrum where the difference in absorbances were appreciable.

Results and Discussion

Absorption spectra of lanthanoid–CTB chelates

The studies on the nature of the complexes show that in each of the systems only one chelate is formed under the conditions of experiment. The wavelength of maximum absorption of CTB at pH 6·0 lies at 515 mμ while that of the chelates of rare earths varies between 530 and 545 mμ as shown in Table 1 (Fig. 1 for Yb).
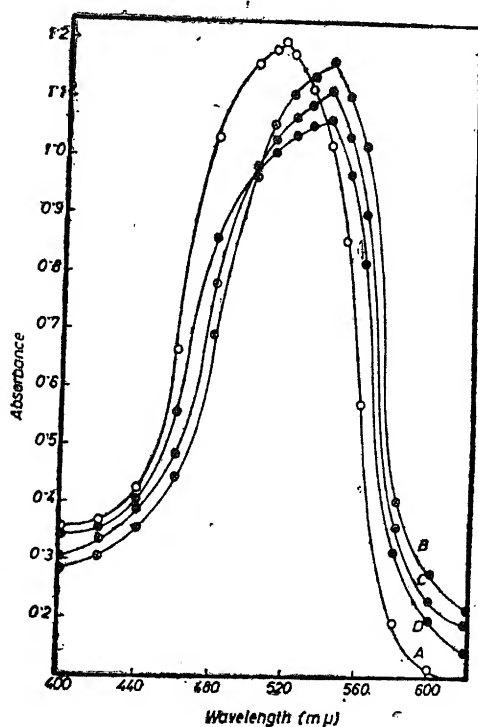
Fig. 1. Absorption spectra of Yb (III)-CTB chelate
Final concentration of the reactants :
    Curve A : CTB = 8·0 × 10⁻⁵M
    Curve B · CTB = 8·0 × 10⁻⁵M YbCl₃ = 16·0 × 10⁻⁵M
    Curve C : CTB = 8·0 × 10⁻⁵M YbCl₃ = 8·0 × 10⁻⁵M
    Curve D : CTB = 8·0 × 10⁻⁵M YbCl₃ = 4·0 × 10⁻⁵M

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Absorption spectra of lanthanoid–CTB chelates at various pH

Mixtures of rare earths and CTB (8.0×10^{-5}M each) were prepared and their absorbances were measured at different pH values, from 400 at 700 mμ. The wavelength maxima thus obtained in each case were plotted against pH and the range of pH within which the λ_{max} remains constant was determined. This pH range was considered to be the range within which the chelates are stable and are shown in Table 1.

Stoichiometry of the Components

Three different methods were applied for determining the stoichiometry of the chelates. The methods used are (*i*) method of continuous variations, (*ii*) mole ratio method, and (*iii*) the slope ratio method. In all the three methods measurements were done at 580 and 600 mμ using solutions of various concentrations. The results show that 1 : 1 (Metal : CTB) chelates were formed in each case (Fig. 2, 3 for Yb).
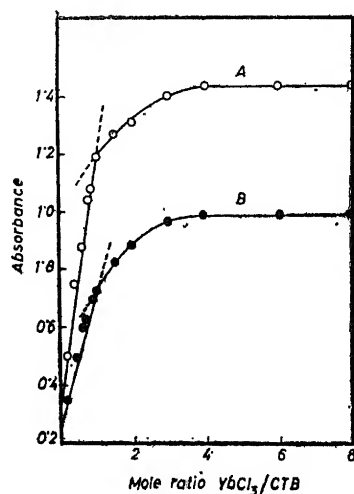
Fig. 2. Determinaiion of the composition of Yb (III)–CTB chelates using mole ratio method.

Final concentration CTB
Curve A = 1.00×10^{-4}M
Curve B = 6.67×10^{-5}M
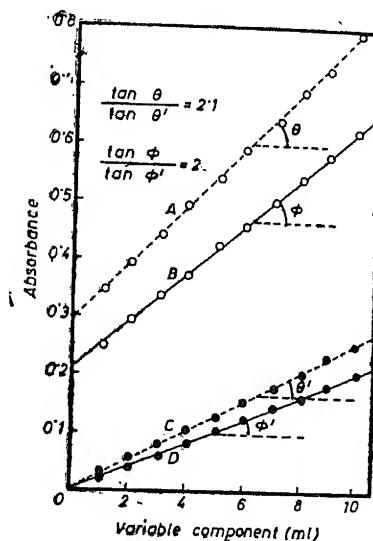
Fig. 3. Determination of the composition of Yb (III)–CTB chelates by the slope ratio method at pH 6.0.
Curve AC 580 mμ
Curve BD 600 mμ
Curve AB CTB in excess, YbCl$_3$ varying
Curve CD YbCl$_3$ in excess, CTB varying
10 ml (4.00×10^{-4}M) excess component + x ml (1.33×10^{-4}M) variabl component + ($15-x$) ml H$_2$O.

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TABLE 1

Characteristics of the lanthanoid—CTB chelates

Chelate	λ_{max} mμ	pH range of stability	Composition M : CTB
Ce (III) – CTB	540	5·5 – 7·5	1 : 1
Pr (III) – CTB	535	5·5 – 7·5	1 : 1
Nd (III) – CTB	540	5·0 – 8·2	1 : 1
Sm (III) – CTB	530	5·0 – 7·5	1 : 1
Eu (III) – CTB	530	4·0 – 7·5	1 : 1
Gd (III) – CTB	530	5·5 – 7·5	1 : 1
Tb (III) – CTB	540	5·0 – 8·0	1 : 1
Dy (III) – CTB	535	5·0 – 8·0	1 : 1
Ho (III) – CTB	545	5·5 – 7 4	1 : 1
Er (III) – CTB	540	5·6 – 7·0	1 : 1
Tm (III) – CTB	540	5·0 – 7·5	1 : 1
Yb (III) – CTB	540	5·0 – 7·5	1 : 1
Lu (III) – CTB	540	5·0 – 7·5	1 : 1

Structure of the CTB chelates of rare earths

It may be of interest to make some suggestions on the position of the chelate ring in the metal chelates formed between CTB and the lanthanoids. The chelates are anionic in nature as has been noted from electrophoretic experim ents and also by the complete adsorption by ion exchange resin Amberlite IR–45 (OH). It is, therefore likely that chelation occurs between the two oxygens in the 1 and 8 positions as shown below.
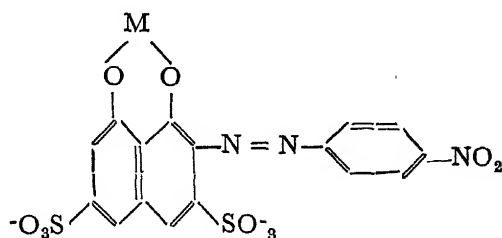
(M stands for rare earths)

Stability constants : The stability constants of the various chelates of the lanthanoids have been calculated by three methods (*a*) method of Dey *et al*, (*b*) method of continuous variations, (*c*) mole ratio method. The values of log K at pH 6·0 and 25°C are given in Table 2.

TABLE 2

Stability constants of lanthanoid–CTB chelates

pH 6·0 ;   Temperature 25°C

Metal chelate	log K by the methods		
	(a)	(b)	(c)
Ce (III) – CTB	4·5 ± 0·2	4·4 ± 0·2	4·8 ± 0·1
Pr (III) – CTB	4·8 ± 0·2	4·7 ± 0·2	4·9 ± 0·1
Nd (III) – CTB	4·8 ± 0·2	5·0 ± 0·2	5·2 ± 0·2
Sm (III) – CTB	4·6 ± 0·1	4·7 ± 0·2	4·8 ± 0·1
Eu (III) – CTB	5·0 ± 0·2	5·0 ± 0·2	5·2 ± 0·5
Gd (III) – CTB	4·5 ± 0·1	4·4 ± 0·1	4·7 ± 0·1
Tb (III) – CTB	4·6 ± 0·3	4·5 ± 0·1	4·5 ± 0·2
Dy (III) – CTB	4·8 ± 0·4	4·7 ± 0·2	4·5 ± 0·2
Ho (III) – CTB	4·7 ± 0·4	4·6 ± 0·2	4·8 ± 0·2
Er (III) – CTB	4·9 ± 0·3	4·8 ± 0·2	4·8 ± 0·1
Tm (III) – CTB	4·7 ± 0·3	5·0 ± 0·2	4·9 ± 0·2
Yb (III) – CTB	4·3 ± 0·2	5·2 ± 0·4	5·3 ± 0·2
Lu (III) – CTB	5·2 ± 0·2	5·6 ± 0·2	5·3 ± 0·1

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Effect of soil and foliar application of urea on yield and quality of wheat

By

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Soil fertility is the capacity of soil to provide nutrients in adequate amounts and in proper balance for plant growth. The presence of large quantities of nutrients in a particular soil does not necessarily mean the high productivity of that soil. These nutrients may not be available to plants due to various factors such as physical condition of the soil, soil pH, limited soil moisture content etc.

Application of fertilizers through foliage has recently proved to be the most efficient method of supplying nutrients to plants both abroad (Finney *et al,* 1957 ; Thorne, 1957 and Wittwer, *et al.,* 1963) and in India (Koraddi and Seth, 1964 and Seth and Prasad, 1965).

Mexican wheats which have been introduced to our country recently, require heavy doses of nitrogenous fertilizers. Unfortunately production of nitrogenous fertilizers in our country is very low and is not able to meet the requirements of crop growers. Foliar fertilization of crops, therefore, has great promise in India.

In order to study the possibility of economising in the use of nitrogenous fertilizers on Mexican wheats, a field trial was laid out at the Agronomy Division Farm, Indian Agricultural Research Institute, New Delhi during the Rabi season 1965-66.

Materials and Methods

The soil of the field was sandy loam of the alluvium type and was of medium fertility. The total nitrogen was 1791 kg/ha, available phosphorus was 35 kg/ha, and the pH of the soil was 7·5.

Soil application of nitrogen, phosphorus, and potassium in the forms of urea, single superphosphate and muriate of potash, respectively was done at the time of sowing of wheat crop. A basal dressing of 50 kg each of phosphorus and potassium per hectare was given to each plot. There were three doses of nitrogen applied in soil as well as through foliar spray viz. 50, 100 and 150 kg per hectare. Urea was applied through foliar spray on wheat starting from 47 days after sowing at jointing and booting stages and also midway between these two stages. The interval between three and two sprays was 7 and 13 days respectively. The concentration of the urea solution was prepared at three percent.

Wheat variety Sonora 63, a semi-dwarf wheat introduced from Mexico was sown on November 5, 1965 and harvested on April 5, 1966. The experiment was laid out in a randomized block design with four replications and ten treatments. The plot size was 10 m × 5 m.

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Experimental Results :

Yield : Data given in Table 1 show that there was a significant influence of nitrogen on yield of wheat grain. There was also a significant effect of different rates of nitrogen on yield of wheat. Complete soil application or half soil plus half foliar application of nitrogen at 100 kg per hectare resulted in additional yields of 6·7 or 11·0 quintals of wheat grain respectively when compared with 50 kg of nitrogen per hectare applied in soil or with 50 kg of nitrogen per hectare applied half in soil and the other half on foliage in two or three equal sprays.

TABLE 1.

Yield, response per kg of nitrogen, length of earhead, thousand grain weight, grain protein %, phosphorus % and protein in Q/ha of wheat as affected by nitrogen application.

Kg N/ha	Soil	Spray	Yield Q/ha	Response in kg/kg/ N	Length of earhead cm	Thousand grain weight gm.	Grain Protein %	Grain Phosphorus %	Grain Protein Q/ha
50	Full	—	27·9	22·0	8·57	38·74	9·52	0·82	2·6
100	Full	—	34·6	17·7	9·25	39·45	11·00	0·86	3·8
150	Full	—	37·8	13·9	9·40	40·98	11·74	0·87	4·4
50	½	½ Two	28·3	22·8	9·20	39·08	10·13	0·88	2·9
50	½	½ Three	29·7	25·6	8·92	39·85	10·15	0·86	3·0
100	½	½ Two	39·3	22·4	9·63	40·49	11·97	0·98	4·7
100	½	½ Three	40·7	23·8	10·32	40·40	12·27	0·97	5·0
150	½	½ Two	37·2	13·5	9·63	40·30	12·15	0·97	4·5
150	½	½ Three	35·5	12·4	9·93	39·97	12·34	0·97	4·4
Control (No nitrogen)			16·9		6·27	37·30	8·94	0·75	1·5
S. Em.			±1·2		±0·29	±0·40	±0·30	±0·03	
L. S. D. at 5%			3·5		0·84	1·16	0·87	0·09	

Application of 100 kg of nitrogen per hectare half in soil and the other half on foliage in three equal sprays resulted in a significant increase in grain yield (by 6·1 quintals per hectare) when compared with the same dose of nitrogen applied completely in soil at sowing time. There were no significant differences between three and two foliar sprays of urea on wheat. In fact three foliar sprays of urea resulted in slightly higher yields than two sprays at all the doses except at the dose of 150 kg of nitrogen per hectare. Application of urea at 150 kg of nitrogen per hectare half in soil and half through foliage resulted in a reduction in the yield of wheat when compared with soil application at the same dose.

Data on the quantity of wheat grain produced per kg of nitrogen added, are shown in Table 1. Data indicate that 50 kg of nitrogen per hectare applied half in soil and the other half on foliage in three foliar sprays resulted in a maximum quantity of wheat grain *i. e.* 25·6 kg per kg of nitrogen added. However, soil application of nitrogen at 150 kg per hectare and 100 kg/ha resulted in only 13·9 and 17·7 kg of grain per kg of nitrogen added.

Length of earhead : Data given in Table 1 indicate that there was a significant effect of nitrogen application on length of earhead. A maximum length of 10·32 cm of wheat earhead was produced with the application of 100 kg of nitrogen per hectare half applied in soil and the other half on foliage in three equal sprays. This length of earhead was 4·05 cm more than the length observed in case where nitrogen was not added. Foliar application of nitrogen (three sprays) in addition to soil application (100 kg N/hectare) resulted in significantly longer earhead than produced with complete soil application of 100 kg of nitrogen per hectare or with 150 kg of nitrogen per hectare. There were no appreciable differences in lengths of earheads obtained due to two or three foliar sprays.

Thousand grain weight : Data on one thousand grain weight of wheat are shown in Table 1. There was a marked influence of nitrogen application on one thousand grain weight of wheat. Application of nitrogen in soil at 100 kg per hectare did not result in significant increase in one thousand grain weight when compared with 50 kg of nitrogen per hectare, but when the dose of nitrogen was further increased to 150 kg, there was a significant increase in one thousand grain weight. There was a slight increase in thousand grain weight due to foliar application of nitrogen (three sprays) in combination with soil application at 100 kg per hectare when compared with 50 kg of nitrogen applied in a similar way, but when the dose was increased to 150 kg of nitrogen, there was decline in one thousand grain weight. Application of 100 kg of nitrogen half in soil and the other half on foliage in three equal sprays resulted in greater, but not significantly, one thousand grain weight than produced with the same dose of nitrogen applied in soil. There were no appreciable differences between two and three foliar sprays.

Protein percentage of grain : Data on protein percentage of wheat grain shown in Table 1 indicate that there was a significant effect of nitrogen on protein percentage of wheat grain for all the methods of application. There was a significant increase in protein percentage of wheat grain with 100 kg. of nitrogen per hectare half applied in soil and the other half on foliage when compared with lower dose *i.e.* 50 kg per hectare, but there was no appreciable increase in protein percentage of wheat grain with a high dose of nitrogen *i.e.* 150 kg per hectare. Application of nitrogen at 100 kg per hectare half in soil and the other half on foliage (three foliar sprays) resulted in a significant increase in protein percentage (by 1·27%) when compared with the same dose of nitrogen applied in soil. The protein percentage of 12·27 obtained with 100 kg of nitrogen per hectare applied half in soil and the other half on foliage in three equal sprays was 3·33 % higher than that obtained in case where nitrogen was not added to the crop. There were no significant differences between two and three foliar sprays of nitrogen with regard to protein percentage of wheat grain.

Grain protein production : The quantity of grain protein produced per hectare was calculated and its data are given in Table 1. These data show that application of nitrogen at 100 kg per hectare half in soil and the other half on foliage in three equal sprays resulted in the production of maximum quantity of grain protein *i.e.* 5·0 quintals per hectare. This was considerably more than the quantity of protein produced by applying 100 or 150 kg of nitrogen per hectare in soil. Although the maximum wheat protein percentage of 12·34 was obtained with the application of nitrogen at 150 kg per hectare half in soil and the other half on foliage in three sprays, yet the total protein produced per hectare was short of maximum with this treatment.

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Phosphorus percentage of grain : Data given in Table 1 show that there was a great influence of nitrogen application on phosphorus content of wheat grain. Higher doses of nitrogen through foliar spray resulted in greater phosphorus content of wheat grain. Application of nitrogen at 100 kg per hectare half applied in soil and the other half on foliage (three equal sprays) resulted in significant increases (0·11 % and 0·10% respectively) in phosphorus percentages of wheat grain when compared with the same dose of nitrogen or with higher dose of nitrogen *i.e.* 150 kg per hectare applied in soil. The phosphorus percentage of wheat grain was 0·97 with 100 kg of nitrogen per hectare applied half in soil and the other half on foliage in three equal sprays and this was 0·22% more than that obtained with the treatment where nitrogen was not applied. There were no appreciable differences between two and three foliar sprays of nitrogen with regard to phosphorus content of wheat grain.

Discussion

Foliar sprays of urea in addition to an equal quantity of the fertilizer added in soil at sowing time at 100 kg nitrogen per hectare to wheat crop resulted in considerable increases (141·4% or 17·8%) in wheat yields when compared with the control plot or with the treatment where the same quantity of fertilizer was applied in soil. This is in confirmity with the findings of Thorne, 1957 : Finney *et al.*, 1957 ; Vainatheyn, 1962 ; and Seth and Prasad, 1965.

The increase in grain yield due to foliar spray of urea in addition to its soil application might be due to more efficient utilization of nitrogen by the wheat plant through this method. This is evidenced by the fact that foliar spray resulted in a greater production of wheat grain per kg. of nitrogen added half in soil and the other half on foliage than when nitrogen was added completely in soil. The higher efficiency of foliar applied nitrogen has also been reported by Vainatheyn (1962) in wheat, and Seth and Prasad (1965) in barley. There was also a clear indication of the fact that utilization of nitrogen by wheat plant was greater at lower doses than at higher ones either when applied in soil or when applied on foliage. This was also observed by Vainatheyn, 1962 and Seth and Prasad, 1965.

The longer earhead and greater weight per thousand grains due to foliar spray of urea resulted in higher wheat yields. Increase in the dose of nitrogen from 100 to 150 kg. per hectare when applied both in soil and on foliage resulted in a decrease in the yield of wheat. This decrease in yield might be due to the application of a higher than optimum dose of nitrogen to wheat crop.

The fact that application of urea at 100 kg. nitrogen per hectare half in soil and the other half on foliage resulted in about 3 quintals more of wheat grain than at 150 kg. of nitrogen all applied in soil at sowing time, clearly shows the superiority of foliar feeding of nutrients. There is a great possibility of increasing the yields of Mexican wheat varieties and at the same time economising in the use of fertilizers by adopting foliar fertilization method.

In these studies it was also observed that the quality of wheat grain with respect to protein content considerably improved due to nitrogen application. Other workers like, Seth *et al*, 1960 ; Seth, 1963 ; and Seth and Prasad, 1965 have also found improvement in protein content of wheat and other cereal grains due to foliar spray of nitrogen. Moreover, the total quantity of protein per hectare, considerably increased (5·0 quintals per hectare) due to foliar application of urea at 100 kg. nitrogen per hectare in three equal sprays when compared with complete soil application of urea at the same dose in which case it was only 3·8 quintals

per hectere. This was due to the fact that foliar spray resulted in both higher yields and greater protein content of wheat grain.

Similarly, there was also a marked improvement in the phosphorus content of wheat grain due to the foliar application of urea. This is in confirmity with the results of Grechukhina and Timofeeva, 1961 who obtained high phosphorus content of wheat grain with foliar spray of nitrogen. Higher levels of nitrogen application resulted in increased phosphorus content of wheat grain. This is in accord with Shimagami and Kushizaki, 1962.

Foliar spray in these studies provided a more rapid utilization of nutrient by fast growing wheat variety which was also a heavy feeder of nitrogen and consequently the yields of wheat increased considerably with less quantity of the fertilizer.

Summary

A study was conducted to evaluate the relative efficiency of soil and foliar application of urea on yield and quality of wheat. The experiment was laid out in a randomised block design with 10 treatments replicated four times. Phosphorus and potassium were applied at the rate of 50 kg. per hectare as basal dressings. Nitrogen at rates of 50, 100 and 150 kg. per hectare was applied half in soil at the time of sowing and the other half on foliage. The foliar sprays were made in two and three equal instalments. From the results of this study it was concluded :

1. Foliar spray of urea at 100 kg. nitrogen per hectare half in soil and the other half on foliage in three equal instalments resulted in greater grain yield, length of earhead and one thousand grain weight than the same dose of nitrogen applied in soil.

2. There were no significant differences between two and three foliar sprays of urea.

3. The efficiency of nitrogen utilization by wheat plant was greater at lower doses than at higher ones.

4. Protein and phosphorus contents of wheat grain were considerably increased due to foliar spray of nitrogen and also due to increased levels of nitrogen application.

5. The quantity of grain protein per unit area was more due to foliar spray of urea than due to soil application method.

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Studies on the recovery of fertilizer nitrogen by Oats as affected by nitrogen fertilization levels and Soil Moisture Supply[1]

By

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Introduction

The immediate value in plant growth of a nutrient added to the soil depends in the first place on the extent to which it has been taken up by plants. Studies on the recovery of the applied nutrient by plants are therefore of obvious importance. The utilization of a nutrient from a fertilizer source has often been determined by subtracting the amount of that nutrient in unfertilized plants from that in the fertilized ones. This, the 'difference method', has drawbacks that on one hand the plants grown under the condition of deficient nutrient supply are compared with those amply supplied with that nutrient and on the other hand the effect of the applied fertilizer on the availability of that nutrient already present in soil is not taken care of. Use of a labelled source, however—be the label a radioactive or a stable isotope—offers the possibility that through the application of the principle of isotopic dilution the simultaneous contribution of two sources of a nutrient be determined without above limitations. Although this 'isotopic method' has also its own shortcomings particularly due to isotopic exchange reactions and fixation (Michael and Machold 1957, Russell *et al*, 1954, Scheffer and Ulrich 1958), its results are usually more reliable than those of the difference method (Michael and Machold 1957).

Utilization of fertilizer nitrogen by plants has been investigated by using the stable isotope 15 N. Most of such studies have shown that the recovery of fertilizer nitrogen by the main crop is rather low (Bartholomew *et al*, 1950, MacVicar *et al*, 1950, Turtschin *et al*, 1960, Viets 1960). This paper reports the results of an experiment which was conducted to study the utilization of fertilizer nitrogen through oats (*Avena sativa*) as affected by the nitrogen fertilization levels and the soil moisture supply. The experiment also aimed at studying how the difference method would compare with the isotopic method in determining the nitrogen recovery under the conditions of above variables.

Methods and Materials

The experiment consisted of a pot-culture of oats in 2 litre beakers having a mixture of 0·75 kg fine-quartz-sand and 1 kg of a loam soil. The soil was from northern Blackforests (W. Germany) containing 0·239 % total nitrogen, 0·0'3% lactate soluble P_2O_5 and 0·026% lactate soluble K_2O and showing a pH value of

6·0 and a moisture content of 22·7% at 0·3 atm and 9·8% at 15 atm tensions on the dry weight basis. In a factorial design, all combinations of three levels of nitrogen, N_0, N_{150}, N_{300} (i.e., 0, 150 and 300 mg nitrogen per pot), and two moisture regimes, 'moist' and 'dry', (corresponding to irrigation when respectively 50% and 80% of the available water were exhausted) were tried. Each pot received an uniform supply of 00 mg P_2O_5 (as finely powdered $CaHPO_4$ mixed with dried soil and 250 mg K_2O (as K_2SO_4 in no nitrogen pots and as KNO_3 in the rest). The balance of nitrogen, as necessitated by the treatments, was supplied through $Ca(NO_3)_2\,4H_2O$. To label the fertilizer nitrogen, 20% of the total amount was supplied through a KNO_3 salt containing 95·7 per cent excess 15N. The salts supplying nitrogen and potassium were mixed with the soil as solutions before planting. The pots, initially planted with 15 seeds of oats (var. Carsten's Phonix), finally carried 12 plants each. The experiment was terminated 70 days after sowing (i.e., 45 days after the onset of moisture regime treatments) by harvesting the whole shoots, which were immediately dissected into leaf, stem and ear, freeze-dried, weighed and prepared for analysis. The content of total nitrogen in the dried plant material was determined by micro Kjeldahl procedure and the nitrogen thus obtained in ammonium form was converted into N_2 gas Rittenberg tubes as described by Peach and Tracey (1956) for 15N-assay. From the arc-emission-spectrograph of this gas, the frequency of 15N in the total nitrogen was calculated by comparing the optical densities of $28N_2$ and $29N_2$ lines (corresponding to 3159 Å and 3162 Å, respectively) as described by Schumacher (1965). Per cent recovery of fertilizer nitrogen by isotopic method (R_i) and by difference method (R_d) were calculated as follows :

$$R_i = \frac{\text{frequency of 15N in plant nitrogen}}{\text{frequency of 15N in fertilizer nitrogen}} \times 100 \text{ and}$$

$$R_d = \frac{\left[\begin{array}{c}\text{nitrogen-uptake by}\\ \text{fertilized plants}\end{array}\right] - \left[\begin{array}{c}\text{nitrogen-uptake by}\\ \text{unfertilized plants}\end{array}\right]}{\text{nitrogen added to the soil as fertilizer}} \times 100$$

Experimental Findings

The main effects of the levels of nitrogen and moisture regimes as well as their combinations on the dry matter yield, total nitrogen uptake and utilization of fertilizer nitrogen have been summarised in the Table.

The mean effect of nitrogen fertilization on the dry matter yield was not significant. The yield was markedly low at 'dry' regime as compared to 'moist' one. Increasing rates of nitrogen fertilization resulted in decreasing yield increments at 'moist' regime whereas at 'dry' moisture regime nitrogen fertilization caused reduction in yield as compared to no nitrogen control.

Total nitrogen uptake increased as the nitrogen supply was increased, the rise due to the first dose (i.e., N_{150}) being higher than due to the second one (i.e., N_{300}). At 'dry' regime the total uptake was considerably lesser than at the 'moist'; however, this effect of soil moisture regime was not as marked as its effect on dry matter production.

Whereas the absolute amount of fertilizer nitrogen recovered by plants increased as the fertilization rate was raised, the per cent recovery of applied nitrogen decreased. The recovery was conspicuously low at 'dry' moisture regime. A comparison of recovery data as worked out by isotopic method with those determined by difference method reveals that the latter method underestimated

the recovery values. The magnitude of this underestimation was greater at higher fertilizer dose in comparison to the lower one and at 'dry' regime as compared to 'moist' regime.

TABLE

Effect of levels of nitrogen and moisture on the dry matter production, total nitrogen removal and recovery of fertilizer nitrogen by oats shoots

Treatments	Dry matter yield g/pot	Total N removed mg/pot	Per cent N Derived from fertilizer (isotopic method)	N (mg/pot) removed from the fertilizer as estimated by		Per cent recovery of fertilizer nitrogen as estimated by		b/a
				Isotopic method	Difference	Isotopic method (a)	Difference method (b)	
Levels of N (averaged over moisture regimes) :								
No nitrogen	9·4	145·6	–	–	–	–	–	–
150 mgN/pot	9·7	193·1	35·3	68·7	47·6	45·8	31·7	0·69
300 mgN/pot	9·7	209·1	48·0	101·0	63·5	33·7	21·1	0·62
L. S. D. 5%	*	7·1	1·3	6·7	8·8	3·1	3·8	
Moisture regimes (averaged over levels of nitrogen) :								
Moist	11·9	209·6	43·2	104·2	88·8	48·6	42·1	0·86
Dry	7·3	155·5	40·1	65·5	22·2	30·8	10·7	0·34
L. S. D. 5%	0·5	6·6	1·3	6·7	8·8	3·1	3·8	
Moisture regime × nitrogen levels :								
Moist, no nitrogen	11·2	150·4	–	–	–	–	–	–
„ 150 mg N/pot	12·2	225·7	36·9	83·4	75·3	55·6	50·2	0·91
„ 300 mg N/pot	12·3	252·7	49·4	124·9	102·3	41·6	34·1	0·82
Dry, no nitrogen	7·5	140·8	–	–	–	–	–	–
„ 150 mg N/pot	7·2	160·6	33·5	53·9	19·8	35·6	13·2	0·37
„ 300 mg N/pot	7·1	165·8	46·6	77·1	24·6	25·7	8·2	0·32
L. S. D. 5%	0·9	11·5	*	9·4	12·4	*	5·4	

*Not significant

Discussion

A lack of substantial growth response of plants to nitrogen fertilization could be attributed to the presence of appropriate amount of nitrogen in the soil. Due to the luxury consumption of available nitrogen, the amount of total nitrogen taken up by plants increased as the level of nitrogen fertilization was raised in spite of little increase in the dry matter production. The values for the per cent recovery of fertilizer nitrogen, as determined by difference method or isotopically, fall with in the range of those reported by others. The percentage of applied nitrogen recovered by plants decreased as the level of nitrogen fertilization was raised. Most probably the limiting effect of some other growth factors became accentuated at the higher level of nitrogen fertilization so that increased amount of available nitrogen could not be utilized by the plants proportionate to its supply. Very low recovery values for 'dry' moisture regime were primarily due to highly restricted growth resulting from the insufficient moisture supply for plants at this regime.

The two methods of calculating recovery of fertilizer nitrogen gave values which differed considerably from each other. Although the nitrogen utilization values as worked out by isotopic method could also be lower than the actual ones because of microbial immobilization of fertilizer nitrogen and accelerated mineralisation of soil nitrogen upon the addition of fertilizer in the soil, these values are more reliable than these yielded by difference method as after all 'the label in the plant would come from the applied fertilizer only' (Michael and Machold 1957). The isotopic method can, therefore, be taken as a standard for comparison. The most conspicuous fact that emerged out of this comparison is that the difference method very much underestimated the values for fertilizer utilisation particularly under the conditions of lower moisture supply. Under 'dry' moisture regime the recovery values for fertilizer nitrogen estimated by difference method were almost one third of that by isotopic method. This discrepancy seems to arise due to the basic assumptions on which the difference method works. Here it is assumed that the amount of soil nitrogen taken up by plants would be same both in the presence as well as in the absence of a nitrogen fertilizer. The validity of this assumption is naturally limited, as is evident from several works (Behrens 1955, Kurtz et al, 1961, Michael and Machold 1957). This assumption could perhaps hold under such situation, when with increasing rates of nitrogen fertilization a linear increase in the total nitrogen uptake occurred proportionate to the increased total nitrogen supply in the soil. If such an increase were not to occur, the assumption would be invalid because in the presence of fertilizer nitrogen, then, a relatively smaller amount of soil nitrogen would be taken up by plants, as logically the plants should cover their nitrogen needs from soil and fertilizer sources proportionate to the amount of the available nitrogen present in each of these sources. The result would be that while calculating the recovery by difference method a value for soil nitrogen bigger than the actual one would be subtracted from the total nitrogen and consequently a lower value for recovery of fertilizer nitrogen would be obtained. The results of present experiment could serve as an example supporting this contention. In this study, as the level of nitrogen fertilization was raised, the total nitrogen uptake did not increase linearly but at a diminishing rate and the marginal increments were particularly smaller under the 'dry' regime as compared to 'moist one'. The values for fertilizer nitrogen utilization as determined by difference method were, therefore, lower in comparison to isotopic method and the magnitude of the deficit was particularly greater at drier moisture regime and higher level of nitrogen fertilization. It is probable that under 'dry' moisture regime conditions, as the level of nitrogen fertilization was raised, the root growth was adversely affected, in consequent of which the root system of fertilized plants could not take up as much soil nitrogen as that of the unfertilized control ; hence, while calculating nitrogen utilization by difference method a much bigger amount for soil nitrogen was deducted than the actual one, and the recovery values worked out to be very low.

Summary

In a pot culture experiment with oats the recovery of fertilizer nitrogen as affected by the levels of nitrogen fertilization (i.e., 150 and 300 mg nitrogen as nitrate per kg soil) and moisture regime (i.e., 'Dry' and 'Moist' regimes, corresponding respectively to giving irrigation when 80% and 50% of the available soil moisture were exhausted) was studied using fertilizer nitrogen labelled with 15N. The recovery, ranging from 25.7% to 55.6%, was decreased due to increase in level of nitrogen fertilization and due to drier moisture regime. As compared to isotopic method the difference method of determining nutrient utilization yielded lower

values which ranged from 8·2% to 50·2% depending on level of nitrogen fertilization and moisture supply. The underestimation of the recovery values was particularly greater in magnitude at higher level of nitrogen fertilization and 'drier' moisture regime. The possible reasons for such behaviour are discussed.

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Effect of Algae on the solubilization of sparingly soluble phosphates

By

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The quantitative importance of blue-green algae as nitrogen fixers is fairly well established and in certain tropical soils nitrogen fixation by blue-green algae can undoubtedly make a major contribution to soil fertility. The idea, however, that algae liberate extracellular products is not unfamiliar. In 1908, Putter (1) suggested that algae liberate, directly into surrounding water, a large proportion of the materials, produced in photosynthesis. The extracellular products of algae as complex forming substances are of much importance. Many organic substances including acids, amino acids and polypeptides, possess the property of complexing or chelating inorganic or organic ions and thus considerably modifying their properties (2). The chelating properties have been best demonstrated for the extracellular polypeptides of Anabaena (3).

In the present paper an attempt has been made to find the effect of algal growth and their extracellular products on solublization of various sparingly soluble phosphates. The effect of two blue-green algae *viz.* Anabaena neviculoides and tolypothrix tenuis and a green algae chlorella vulgaris on the phosphatic materials has been investigated.

Phosphatic source	Abbreviation used	%P_2O_5
Tata Basic slag	TBS	7·786
German Basic slag	GBS	17·401
Kulti Basic slag	KBS	3·467
Durgapur Basic slag	DBS	3·766
Tricalcuim phosphate	$Ca_3(PO_4)_2$	45·8
Aluminium phosphate	$AlPO_4$	50·7
Ferric phosphate	$FePO_4$	37·95

Experimental

The study consist of two parts :

1. *Solution :* Different phosphates at the rate of 0·1% P_2O_5 were added to 300 ml conical flasks containing 150 ml of culture media of the following composition.

	Medium for Anabaena and Tolypothrix	Medium for chlorella
	(Amount per litre)	
KNO_3	0·2 gm	Nil
NH_4NO_3	Nil	0·2 gm.
K_2HPO_4	0·2 gm.	0·2 gm.
$MgSO_4 \cdot 7H_2O$	0·2 gm.	0·2 gm.
$CaCl_2$	0·1 gm.	0·1 gm.
$FeCl_3$ (1%)	2 drops	2 drops

The flasks were plugged with cotton and the whole assemblage was sterilized. A few cells of algae were inoculated and it was exposed to 100 watt. bulb for a period of 100 days. After the required period, the material was filtered through Gooch crucible and the final volume raised to 250 ml. The filterate was analysed for its P O content clorimetrically (Hydroquinon-Sod. Sulphite method).

2. *Soil* : 200 gms (passed through 60 mesh sieve) of Alluvial Sandy-loam soil from the village Nagina, Hariana (Total P_2O_5 pH 7·6) was thoroughly mixed with different phosphatic materials (0·1 % P_2O_5), inoculated and incubated in bottles at room temperature under a 100 watt electric bulb. 40 % moisture was maintained for 85 days and then for 15 days the moisture content of the soil was allowed to evaporate at room temperature. 100 days the soil was air dried in enamelled dishes. It was analysed for its P_2O_5 content by the method described by Arrhenius (4).

Results and Discussion

The results of the experiment have been summarized in the following table.

| | | Culture media | | Soil | |
		% P_2O_5	% Difference from control	% P_2O_5 (2 % citric acid soluble)	% Difference from control
1.	TBS	2·001	–	0·0672	–
2.	TBS + Chlorella	3·334	1·333	0·0724	0·0054
3.	TBS + Anabaena	3·933	1·932	0·0704	0·0032
4.	TBS + Tolypothrix	4·172	2·171	0·0762	0·0090
5.	GBS	4·767	–	0·0707	–
6.	GBS + Chlorella	4·703	–·064	0·0645	–0·0066
7.	GBS + Anabaena	4·535	·0·232	0·0641	–0·0062
8.	GBS + Tolypothrix	4·465	–0·302	0·0652	–0·0055
9.	KBS	1·102	–	0·0402	–
10.	KBS + Chlorella	2·098	0·996	0·0415	0·0013
11.	KBS + Anabaena	1·803	0·701	0·0418	0·0016
12.	KBS + Tolypothrix	2·031	0·929	0·0424	0·0022
13.	DBS	1·503	–	0·0569	–
14.	DBS + Chlorella	1·566	0·063	0·0582	0·0013
15·	DBS + Anabaena	2·358	0·855	0·0604	0·0035
16.	DBS + Tolypothrix	1·903	0·400	0·0614	0·0045
17.	$Ca_3(PO_4)_2$	5·133	–	0·0669	–
18.	$Ca_3(PO_4)_2$+ Chlorella	2·402	0·569	0·0698	0·0029
19.	$Ca_3(PO_4)_2$+Anabaena	3·200	1·067	0·0708	0·0039
20.	$Ca_3(PO_4)_2$+Tolypothrix	3·733	1·600	0·0727	0·0058
21.	$AlPO_4$	1·766	–	0·0397	–
22.	$AlPO_4$ + Chlorella	1·834	0·068	0·0415	0·0018
23.	$AlPO_4$ + Anabaena	2·031	0·265	0·0421	0·0024
24.	$AlPO_4$ + Tolypothrix	2·137	0·371	0·0422	0·0025
25.	$FePO_4$	1·638	–	0·0321	–
26.	$FePO_4$ + Chlorella	1·332	–0·306	0·0308	–0·0313
27.	$FePO_4$ + Anabaena	1·437	–0·201	0·0297	–0·0024
28.	$FePO_4$ + Tolypothrix	1·207	–0431	0·0301	–0·0021

The results in the table clearly reveal that the extracellular products secreted during the growth of these algae can solublize the sparingly soluble phosphates and basic slags. The results are better in solution than in soil. Maximum effect is shown in Tata basic slag and tricalcium phosphate. The increase over control by tolypothrix in Tata basic slag and tricalcium phosphate is 2·17 % and 1·6% and by anabaena 1·93% and 1·06% respectively. In soils the order is TBS > $Ca_3(PO_4)_2$ > DBS > $AlPO_4·H_2O$ > KBS.

The increase in crop yield, especially in paddy by inoculation of blue-green algae has frequently been reported and it is attributed to the nitrogen fixed from the atmosphere by these algae. It has been concluded in this paper that a portion of the above reported increase in crop yield may be due to the increase in the availability of phosphates. The decrease in solubility in GBS and $FePO_4·2H_2O$ could not be accounted for. It may be due to little growth of algae in these treatments which take the available P_2O_5 from the source. For it is further noticed that the effect is directly concerned with the intensity of growth of these algae in the media.

Before arriving at any solid conclusion extensive study is needed on this aspect Work on this topic is already under progress.

Summary

Three algae, chlorella vulgaris, anabaena neviculoides and tolypothrix tenuis were grown in pure cultures containing different sparingly soluble phosphates i.e. Tata, German, Durgapur and Kulti Basic Slags, Tricalcium phosphate, Aluminium phosphate and Ferric phosphate (1% P_2O_5). Also soil containing same materials were incubated at room temperature. (40% moisture).

The results indicated that extra cellular products excreted during growth of these algae can increase the solubility of these phosphates. Maximum effect is shown in Tata Basic Slag and tricalcium phosphate. The increase by tolypothrix in Tata basic slag and tricalcium phosphate is 2·17 and 1·6% and by anabeana 1·93 and 1·07% respectively. It is further noticed that the effect is directly concerned with the intensity of growth of the algae in the media.

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Effect of Anabaena neviculoides on nitrogen fixation and Rice yield in presence of Ammonium Sulphate, Municipal compost, wheat straw and basic slag

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Next to wheat rice is the main cereal crop of India. It was observed that in India rice can be grown on the same land for long periods without the addition of manure to the soil (1). Many evidence have now been adduced to show that one of the probable causes for the ability of rice to grow, year after year, in the absence of manure, is due to the fixation of atmospheric nitrogen by the blue-green algae. Growth of these organisms in rice fields is often luxuriant, many of the species concerned have been shown to be nitrogen fixing (2, 3, 4).

In recent years, much importance has been attached to the blue-green algae that develop in great masses in rice fields and it is generally believed that algae take part in the nitrogen cycle in the soil.

The present study was outlined with the view to obtain some information about the influence of organic matter, ammonium sulphate and Tata Basic slag on the activity of specially introduced soil blue-green algae, such as Anabaena neviculoides, in paddy fields.

Experimental

Soil : Surface sample from 0–15 cm depth was collected from the Sheila Dhar Institute Lawn. (Silt loam), dried in the shade and ground to pass through 4 mm mesh sieve. Sieved soils were mixed very thoroughly for potting.

Potting of Samples : Uniform earthenware pots (without any hole) lined with black bituminus, non-chippable paint were packed with 5 Kg of soil.

Addition of nutrients other than Phosphorus and Nitrogen : With the exception of phosphorus and nitrogen, other nutrients which are considered essential for the plant growth were supplied at the following rates :

Nutrient	Forms in which applied	Dose per acre
Potassium	Potassium sulphate	80 lbs K_2O
Magnesium	Magnesium sulphate	20 lbs Mg
Iron	Ferrous sulphate	10 lbs Fe
Manganese	Manganese chloride	20 lbs Mn
Zinc	Zinc chloride	25 lbs Zn
Copper	Copper sulphate	15 lbs Cu
Molybdenum	Ammonium molybdate	2 lbs Mo
Boron	Borax	5 lbs Bo

These nutrients and ammonium sulphate were added in the form of solution. Municipal compost (well decomposed) and powdered Tata basic slag were added as such. Wheat straw (powdered) was incorporated 30 days before transplanting of paddy seedlings. Each pot contained 4 plants.

Two groups (A and B) of pots were set up for receiving the different materials shown in Table 1.

Inoculation with Anabaena neviculoides* in pots of group B were carried out a week after sowing.

TABLE 1

Materials added to Pots

Pot No.		Ammonium sulphate (A/S)	City compost (Comp.)	Wheat straw (Str.)	Tata Basic slag (TBS) (P)
Group A	Group B				
Not-inocu-lated	Inocu-lated	21·5% N	1·38% N	0·64% N	7·5% P_2O_5
1	13	0	0	0	0
2	14	0	0	0	1P
3	15	0	0	0	2P
4	16	1N	0	0	0
5	17	1N	0	0	1P
6	18	1N	0	0	2P
7	19	0	1N	0	0
8	20	0	1N	0	1P
9	21	0	1N	0	2P
10	22	0	0	1N	0
11	23	0	0	1N	1P
12	24	0	0	1N	2P

1 N = 30 lbs Nitrogen per acre
1 P = 30 lbs P_2O_5 per acre
2 P = 60 lbs P_2O_5 per acre
All treatments were in three replicates and the rate of addition to each pot was calculated on area basis.

All pots were sufficiently irrigated daily to provide a layer of water about $1\frac{1}{2}$ inch above the surface of the soil. The rice plants, when ripe were cut at the surface of the soil. The grains and the straw were separately weighed and ground for total nitrogen determination. The pots were left untouched for a week after which the soil of each pot was taken for the determination of total nitrogen (5).

Results and Discussion

The average yield of grain and straw (calculated on the oven dry basis) obtained from each treatment is recorded in Table 2.

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*Anabaena was propageted in Erlenmayer flasks containing the medium recommended by De(2). After two months the contents of the flasks were beleaded and added at the rate of 5 ml to each pot.

TABLE 2
Average Yields of grain and straw per pot

Treatments		Non-inoculated			Inoculated			
		Pot No.	Grain g.	Straw g.	Pot No.	Grains g.	Straw g.	%increase
0N	0P	1	4·7	7·7	13	5·7	9·1	21·2
0N	1P	2	5·6	10·3	14	7·4	12·2	32·1
0N	2P	3	6·1	11·3	15	8·2	13·5	34·4
1N (A/S)	0P	4	6·4	14·5	16	6·2	12·0	—
1N (A/S)	1P	5	7·0	14·9	17	6·7	13·0	—
1N (A/S)	2P	6	9·1	14·1	18	8·5	13·7	—
1N (Str.)	0P	7	6·1	11·7	19	6·3	14·8	3·3
1N (Str.)	1P	8	6·8	12·7	20	6·5	14·3	—
1N (Str.)	2P	9	8·4	13·1	21	9·7	14·4	15·5
1N (Comp.)	0P	10	6·9	15·5	22	8·4	15·6	21·7
1N (Comp.)	1P	11	7·6	15·0	23	9·6	15·9	26·3
1N (Comp.)	2P	12	9·1	15·8	24	11·4	17·1	25·2

The data show that algae sometimes caused an increase or decrease in both grain and straw. It is interesting to note that the control pots *i.e.* the pots to the soils of which no nitrogen was added, gave, when inoculated remarkably higher yields of both grain and straw.

If inoculation is entirely ignored, the effect of the nitrogenous materials added on grain and straw varies from one material to another, whether Tata basic slag (P_2O_5) exists or not. The effect of micro-organisms on nitrogen fixation is assumed negligible because in the water-logged period, conditions are unfavourable for certain bacteria like *Azotobacter* which are unlikely to be very active at this time (6). De and Datta (7) have also obtained evidence to show that no nitrogen fixation to any measurable extent takes place in rice soils during the dry period and that the conditions occurring in the soil during the said period are not suitable for *Azotobacter* growth. It is mere approximation since some nitrogen must be lost from the soil during the life time of the rice plant (8, 9, 10).

To find the effect of inoculation and overcome above difficulty the gain in nitrogen was calculated.

The gain in nitrogen = (nitrogen in grain and straw + nitrogen left in soil) − (nitrogen orginally present in the soil+nitrogen added).

The data is recorded in Table 3.

It is to be noted that gain in nitrogen was least in the inoculated pots which received ammonium sulphate with or without phosphate (TBS). It is also well established (11, 12, 13, 15) that little or no nitrog·n is fixed in the presence of ammonia since most of the nitrogen required by these organisms is obtained from the ammonical fertilizers applied to the soil. Consequently the crop is more or less deprived of the nitrogen it needs and hence the yield is lowered (Table 2). It is also supported by the nitrogen taken in per cent of added nitrogen (Table 3).

Table 3 also shows that nitrogen fixation in the inoculated pots was considerably stimulated by compost additions obviously because the algae were amply supplied with CO_2 liberated through its decomposition. This agrees with the results obtained by De and Sulaiman and El Fadl *et al.* (14, 13). This received further support from the results obtained with straw. But the increase in yield due to inoculation of algae to straw was not much in comparison to compost.

TABLE 3

Gain in Nitrogen (g./Pot)

Treatments	ON 0P	ON 1P	ON 2P	1N (A/S) 0P	1N (A/S) 1P	1N (A/S) 2P	1N (Str.) 0P	1N (Str.) 1P	1N (Str.) 2P	1N (Comp.) 0P	1N (Comp.) 1P	1N (Comp.) 2P
Pot No.	1	2	3	4	5	6	7	8	9	10	11	12
Initial Soil N	3·560	3·560	3·560	3·560	3·560	3·560	3·560	3·560	3·560	3·560	3·560	3·560
N. Added	—	—	—	0·075	0·075	0·075	0·075	0·075	0·075	0·075	0·075	0·075
Sum	3·560	3·560	3·560	3·635	3·635	3·635	3·635	3·635	3·635	3·635	3·635	3·635
N. Removed	0·094	0·118	0·128	0·148	0·157	0·177	0·130	0·142	0·165	0·159	0·165	0·187
N. Left in the soil	3·460	3·431	3·437	3·462	3·468	3·452	3·499	3·496	3·483	3·482	3·481	3·446
Sum	3·554	3·549	3·565	3·610	3·625	3·629	3·629	3·638	3·648	3·641	3·646	3·633
Gain in N	—	—	0·005	—	—	—	—	0·003	0·013	0·006	0·011	—
N. taken in % of N. Added	—	—	—	72·000	52·000	65·333	48·000	32·000	49·333	86·666	62·666	78·666

Treatments	ON 0P	ON 1P	ON 2P	1N (A/S) 0P	1N (A/S) 1P	1N (A/S) 2P	1N (Str.) 0P	1N (Str.) 1P	1N (Str.) 2P	1N (Comp.) 0P	1N (Comp.) 1P	1N (Comp.) 2P
Pot No.	13	14	15	16	17	18	19	20	21	22	23	24
Initial Soil N	3·560	3·560	3·560	3·560	3·560	3·560	3·560	3·560	3·560	3·560	3·560	3·560
N. Added	—	—	—	0·075	0·075	0·075	0·075	0·075	0·075	0·075	0·075	0·075
Sum	3·560	3·560	3·560	3·635	3·635	3·635	3·635	3·635	3·635	3·635	3·635	3·635
N. Removed	0·113	0·152	0·168	0·133	0·145	0·169	0·155	0·148	0·187	0·177	0·193	0·221
N. Left in the soil	3·496	3·467	3·459	3·511	3·501	3·478	3·529	3·551	3·505	3·506	3·508	3·487
Sum	3·609	3·619	3·627	3·644	3·646	3·647	3·684	3·699	3·692	3·683	3·701	3·708
Gain in N	0·049	0·059	0·067	0·009	0·011	0·012	0·049	0·064	0·057	0·048	0·066	0·073
N. taken in % of N. Added	—	—	—	26·666	0·000	1·333	56·000	0·000	25·333	85·333	54·666	70·666

The nitrogen taken in per cent of nitrogen added $= 100 \times \dfrac{A - B}{C}$, where

A = N removed by crop which received N.
B = N removed by crop which did not received N.
C = N added to soil.

Straw and compost was shown to be unsatisfactory source of nitrogen for rice when applied directly (13). Because the decomposition of compost and straw under the anaerobic conditions prevailing in paddy fields goes on very slowly. But in the present case the results are excellent when well decomposed city compost is added and enough time is given to straw for decomposition in the soil.

The addition of phosphate as Tata basic slag increased yield considerably. The nitrogen fixation by inoculation of anabaena is also stimulated in present of phosphate as Tata basic slag (Table 3). Earlier De and Sulaiman (14) observed that the addition of phosphates to rice soils whether in soluble form as potassium phosphate or in insoluble form as calcium phosphate stimulated the fixation of nitrogen by algae.

It is concluded from this study that the blue-green algae Anabaena neviculoids can be utilized as nitrogen fixer to increase crop yields in paddy soils. The fixation and yields are more when decomposed city compost and wheat straw are applied as organic manures with Tata basic slag. The residual effect on wheat crop is under progress.

Summary

The effect of this alga on the crop yield of rice plants was examined in pots. 30 lbs nitrogen as ammonium sulphate, powdered wheat straw and municipal waste were applied with two rates of phosphorus (30 lbs and 60 lbs P_2O_5 from Tata Basic slag), wheat straw was incorporated 30 days before sowing and other materials just before transplanting of paddy seedlings.

Results obtained indicated that increase in the crop yield as high as 34·4 per cent was achieved by the inoculation of this alga in control pots *i.e.* without any nitrogen treatment.

Inoculated sets in the case of inorganic nitrogenous fertilizer, ammonium sulphate showed no increase over uninoculated ones. The fixation of nitrogen is maximum in the soil manured with phosphated municipal compost and lowest in ammonium sulphate.

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Effect of Sarkanda (*Saccharum munja*) and Coal in presence of Tata Basic slag and calcium ammonium nitrate on crop production

By

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It has long been felt that artifical fertilizers are not only limited in amount but their continuous use affect the permeability and structure of the soil adversely[1,2,3]. Ruschmann[4] holds the view that mineral nitrogenous fertilizers accelerate the breaking down of humus. Similar results have been reported by Dhar[5]. He after extensive investigations suggested the use of organic materials and phosphates for better crops and recuperation of land[6]. Hester and Shelten[7] reported that organic matter has a beneficial effect in keeping the phosphate available for plant use. Extending the use of organic matter and phosphates Karrakar[8] in U.S.A. obtained marked nitrogen fixation and increased corn yield by a mixture of phosphate and manure. Similar results have been reported by Dhar[9] and Levin[10].

Keeping in view the above conclusions, field experiments were carried out on an alluvial sandy loam soil of village Nagina (Hariana) by incorporating various substances like coal, sarkanda (Saccharum munja), Tata basic slag into the soil and their influence in raising the nitrogen status, fertility and crop production was compared with calcium ammonium nitrate (CAN). Crops grown were Bajra and Mung.

Experimental

The land selected for the experiment was as uniform as possible. The soil samples were drawn out from different spots upto a depth of 6 inches for analysis.

Details of layout :

1. Soil alone (control). 2. Soil + Coal. 3. Soil + Tata Basic slag. 4. Soil + Sarkanda. 5. Soil + Coal + Tata Basic slag. 6. Soil + Coal + Sarkanda. 7. Soil + Sarkanda + Tata Basic slag. 8. Soil + Coal + Sarkanda + Tata Basic slag. 9. Soil + Calcium ammonium nitrate. 10. Soil + Calcium ammonium nitrate + Tata Basic slag. 11. Soil + Coal + Calcium ammonium nitrate. 12. Soil + Sarkanda + Calcium ammonium nitrate. 13. Soil + Coal + Calcium ammonium nitrate + Tata Basic slag. 14. Soil + Sarkanda + Calcium ammonium nitrate + Tata Basic slag.

Coal	$2\frac{1}{2}$ tons per acre
Sarkanda	10 tons per acre
Tata Basic slag	50 lbs P_2O_5 per acre
Calcium ammonium nitrate (20%N)	30 lbs Nitrogen per acre
Size of plot	1/60th acre.
No, of replications	3

As the area is dependant on rains, therefore, Sarkanda, Tata Basic slag and Coal were ploughed in directly into the field in the last week of May 1936 inorder to get a well decomposed material before sowing of the crops. The annual rain fall of the area varies from 20–25 inches, most of which is received in June to August. Two more ploughings were given before sowing of the crops. Representative soil samples were taken before sowing and after harvesting the crops and were analysed for different constituents.

TABLE 1

Analysis of Soil and other materials used in the experiment

	Soil	Sarkanda	Coal	T.B.S.
Loss on Ignition	2·9312	89·5234	80·5779	–
Ash	–	10·4766	19·4221	–
HCl insolulbe (Silica)	85·4317	5·7827	8·6343	23·6673
Sesquioxide	6·8213	0·8874	1·9271	33·7431
Fe$_2$O$_3$	3·9143	0·3924	0·8633	11·1912
CaO	0·9760	0·7839	1·4212	29·8652
MgO	0·5683	0·4823	1·6232	4·1094
K$_2$O	0·8768	0·8439	0·8934	0·8601
Total P$_2$O$_5$	0·1281	0·5173	0·3122	7·7863
Available P$_2$O$_5$	0·0081	–	–	4·5411
Total Carbon	0·5003	41·3921	75·2147	–
Total Nitrogen	0·0381	0·6748	1·3873	–
Ammoniacal N	0·0015	–	–	–
Nitrate – N	0·0027	–	–	–

TABLE 2

Analysis of soil before sowing of crops

Treatments	Total Carbon	Total nitrogen	NH$_3$-N	NO$_3$-N	Total P$_2$O$_5$	Available P$_2$O$_5$
1. Soil alone	0·5001	0·0382	0·0015	0·0027	0·1281	0·0081
2. Soil+Coal	0·7081	0·0420	0·0016	0·0028	0·1283	0·0081
3. Soil+TBS	0·4996	0·0381	0·0015	0·0029	0·1432	0·0118
4. Soil + Sarkanda	0·8941	0·0461	0·0023	0·0044	0·1351	0·0107
5. Soil + Coal + TBS	0·7079	0·0420	0·0017	0·0050	0·1356	0·0110
6. Soil + Coal + Sarkanda	1·1025	0·0504	0·0025	0·0047	0·1283	0·0085
7. Soil + Sarkanda + TBS	0·8925	0·0466	0·0047	0·0080	0·1547	0·0168
8. Soil + Coal + Sarkanda + TBS	1·1008	0·0504	0·0050	0·0083	0·1593	0·0167
9. Soil + CAN	0·5000	0·0396	0·0021	0·0033	0·1282	0·0081
10. Soil + CAN + TBS	0·4995	0·0396	0·0023	0·0035	0·1435	0·0119
11. Soil + Coal + CAN	0·7083	0·0434	0·0022	0·0034	0·1283	0·0083
12. Soal + Sarkanda + CAN	0·8940	0·0482	0·0030	0·0051	0·1352	0·0108
13. Soil + Coal + CAN + TBS	0·7079	0·0435	0·0021	0·0035	0·1284	0·0087
14. Soil + Sarkanda + CAN + TBS	0·8924	0·0475	0·0054	0·0086	0·1548	0·0169

TABLE 3

Average yield of Bajra and Mung in Kgs. per plot (1/60th acre)
(Average of three replicates)

Treatments	Bajra		Mung	
	Grain (Kgs)	Straw (Kgs)	Grain (Kgs)	Straw (Kgs)
1. Soil alone (Control)	4·2	19·0	3·8	2·4
2. Soil + Coal	4·9	21·1	4·3	2·8
3. Soil + TBS	5·2	21·4	4·5	2·6
4. Soil + Sarkanda.	6·6	25·5	5·2	3·1
5. Soil + Coal + T.B.S.	5·9	23·7	5·0	3·3
6. Soil + Coal + Sarkanda	7·4	27·7	5·7	3·5
7. Soil + Sarkanda + TBS	8·5	28·4	6·5	4·6
8. Soil + Coal + Sarkanda + TBS	8·5	30·5	6·2	4·0
9. Soil + CAN	5·3	23·5	4·5	3·1
10. Soil + CAN + TBS	6·2	25·6	5·2	3·5
11. Soil + CAN + Coal	6·1	25·6	5·0	3·2
12. Soil + Sarkanda + CAN	7·4	29·3	6·0	3·7
13. Soil + Coal + CAN + TBS	7·2	28·7	5·9	3·6
14. Soil + Sarkanda + CAN + TBS	8·6	32·3	6·8	4·1

TBS = Tata Basic Slag.   CAN = Calcium Ammonium Nitrate.

TABLE 4

Analysis of Variance of yield of Bajra

S. No.	Source of Variation	d.f.	S.S.	M.S.S.	Calculated F	F from the table 5%	1%
1.	Treatments	13	68·92	5·30	66·3	2·15	2·96
2.	Replications	2	0·03	0·01	Highly Significant		
3.	Error	26	2·06	0·08			
4.	Total	41					

C.D. (5%) = 0·453   C.D. (1%) = 0·612

TABLE 5

Analysis of Variance of yield of Mung

S. No.	Source of Variation	d.f.	S. S.	M.S.S.	Calculated F	F from the Table 5%	1%
1.	Treatments	13	22·05	1·68	12·0	2·15	2·96
2.	Replications	2	0·23	0·11	Highly Significant		
3.	Error	26	3·66	0·14			
4.	Total	41					

C.D. (5%) = 0·618   C.D. (1%) = 0·834

[328]

TABLE 6

Analysis of soil after harvesting Bajra

	Treatments	Total Carbon	Total Nitrogen	NH$_3$-N	NO$_3$-N	Total P$_2$O$_5$	Available P$_2$O$_5$
1.	Soil alone	0·4992	0·0379	0·0017	0·0029	0·1265	0·0076
2.	Soil + Coal	0·7076	0·0416	0·0018	0·0030	0·1267	0·0079
3.	Soil + TBS	0·4991	0·0378	0·0018	0·0031	0·1407	0·0195
4.	Soil + Sarkanda	0·8931	0·0466	0·0028	0·0048	0·1325	0·0147
5.	Soil + Coal + TBS	0·7072	0·0416	0·0019	0·0032	0·1327	0·0148
6.	Soil + Coal + Sarkanda	1·1008	000504	0·0030	0·0051	0·1408	0·0196
7.	Soil + Sarkanda + TBS	0·8902	0·0465	0·0052	0·0085	0·1492	0·0248
8.	Soil + Coal + Sarkanda + TBS	0·8991	0·0502	0·0056	0·0089	0·1487	0·0247
9.	Soil + CAN	0·4989	0·0389	0·0024	0.0037	0·1267	0·0079
10.	Soil + CAN + TBS	0·4981	0·0?90	0·0026	0·00?9	0·1408	0·0196
11.	Soil + Coal + CAN	0·7073	0·0428	0·0026	00038	0·1268	0·0079
12.	Soil + Sarkanda + CAN	0·8921	0·0477	0·0035	0·0054	0·1326	0·0147
13.	Soil + Coal + CAN + TBS	0·7068	0·0429	0·0024	0·0039	0·1209	0·0197
14.	Soil + Sarkanda + CAN + TBS	0·8904	0·0471	0·0059	0·0092	0·1488	0·0248

TABLE 7

Analysis of soil after harvesting Mung

	Treatments	Total Carbon	Total Nitrogen	NH$_3$-N	NO$_3$-N	Total P$_2$O$_5$	Available P$_2$O$_5$
1.	Soil alone	0·4974	0·0386	0·0017	0·0033	0·1267	0·0071
2.	Soil + Coal	0·7074	0·0424	0·0021	0·0032	0·1266	0·0081
3.	Soil + TBS	0·4991	0·0377	0 0017	0·0032	0 1411	0·0193
4.	Soil + Sarkanda	0·8937	0·0475	0·0031	0·0049	0·1328	0·0143
5.	Soil + Coal + TBS	0·7068	0·0424	0·0023	0·0032	0·1327	0·0151
6.	Soil + Coal + Sarkanda	1·1006	0·0512	0·0034	0·0u53	0·1408	0·0199
7.	Soil + Sarkanda + TBS.	0·8903	0·0474	0·0057	0·0082	0·1493	0·0243
8.	Soil + Coal + Sarkanda + TBS	0·8993	0·0515	0·0063	0·0088	0·1484	0·0247
9.	Soil + CAN	0·4978	0·0397	0·0021	0·0037	0·1268	0·0076
10.	Soil + CAN + TBS	0·4983	0·0398	0·0024	0·0040	0·1409	.0·0196
11.	Soil + Coal + CAN	0·7079	0·0437	0·0025	0·0041	0·1272	0·0078
12.	Soil + Sarkanda + CAN	0·8923	0·0484	0·0041	0·0059	0·1328	0·0143
13.	Sojl + Coal + CAN + TBS	0·7061	0·0426	0·0022	0·0039	0·1211	0·0204
14.	Soil + Sarkanda + CAN + TBS	0·8896	0·0485	0·0062	0·0098	0·1486	0·0243

Discussion

From the data given in Table 3 it is clearly revealed that the yields of Bajra Mung are higher when extra nitrogen and phosphorus are applied to soil. The increase in yields due to CAN is greater than coal and nearly equals the yields obtained from plots receiving Tata Basic slag. Though the coal treated plots have higher initial nitrogen yet the increase in yield is lower than the plots where CAN was applied. This can be due to the availability of nitrogen in CAN.

Sarkanda when applied two months before sowing undergoes slow oxidation and thus fixes atmospheric nitrogen[5]. Moreover on decomposition it adds nitrogen to the soil ; the fixation of nitrogen being more when phosphate as Tata Basic slag is added (Table 6) The rendering of the fixed nitrogen in the available form seems to be responsible for increasing the yield of Bajra and Mung.

The increase in yield follows the following orders.

Bajra : Treatment Nos. 14 > 8 > 7 > 12 > 6 > 13 > 4 > 10 > 11 > 5 > 9 > 3 > 2 > 1
Mung : Treatment Nos. 14 > 7 > 8 > 12 > 13 > 6 > 10 > 4 > 5 > 11 > 9 > 3 > 2 > 1

The results recorded in Tables 6 and 7 clearly reveal that the nitrogen status of the soil is markedly enhanced when *Sarkanda* and coal are incorporated into the soil, the results are significant when basic slag is used as phosphatic source. From the same tables it is indicated that the availability of phosphate increases when organic matter is incorporated along with Tata basic slag. Moreover marked nitrogen fixation results in addition to an increased crop yield. Phosphate as Tata basic slag acts in two ways ; is increases the decomposition of organic matter and thus more nitrogen is fixed, secondly it stabilises the nitrogen of the soil by forming more stable phospho–proteins.

From the above study it can safely be concluded that Sarkanda which has a wild growth in many areas of Hariana can be profitably used in increasing the nitrogen status and fertility of the soil and the results will be more significant if it is ploughed in Tata basic slag, the waste by product of steel industry or any other phosphatic fertilizer.

Summary

Sarkanda and coal when applied at the rates of 10 tons and $2\frac{1}{2}$ tons per acre respectively in presence of Tata Basic slag and calcium ammonium nitrate were found to increase the yields of Bajra and Mung significantly. It has been observed that Sarkanda as well as coal not only add nitrogen to the soil but when allowed time to decompose can fix appreciable amounts of atmospheric nitrogen. From the study it can safely be concluded that Sarkanda, which has a wild growth in many areas of Hariana, can be utilized to increase crop yields considerably. The results are better when it is ploughed in with Tata Basic slag.

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Photosynthesis of Amino acids *in Vitro*. Part—I. Interaction between glucose and NH_4NO_3 or KNO_3

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Abstract

Aminoacids are photosynthesized by the interaction of glucose and NH_4NO_3 or KNO_3 in the presence of titania, molybdic acid and vanadium pentoxide. The amount and number of aminoacids produced increases when the systems are phosphated with dicalcium phosphate. The aminoacids formation is highly facilitated by the absorption of light.

Introduction

The body structure of all the living things is made up of proteins. The formation of peptides from the aminoacids synthesized on the surface of the earth was difficult to explain because an external source of energy is necessary to effect the combination of two or more aminoacids forming peptides.

Miller[1,2,3] observed the synthesis of aminoacids by passing electric discharge in an atmosphere of mixture of gases such as hydrogen, methane and ammonia. Baly, Heilborn and Hudson[4,5] reported the photosynthesis of aminoacids and nitrogen bases when activated formaldehyde produced photochemically reacts with nitrites.

Dhar and Mukherji[6] obtained small amounts of aminoacids which can be readily detected by ninhydrin by exposing ammonium nitrate, potassium nitrate solutions containing citric acid, tartaric acid and glycerol etc. to light. Pavlovskaya and coworkers[7] observed the formation of aminoacids by the action of ultra violet light on the solution of formaldehyde and ammonium salts in the presence of adsorbents.

Deschreider[8] obtained aminoacides by exposing to ultra-violet rays a mixture containing succinic acid, maleic acid or propionic acids and ammonia, ammonium carbonate or ammonium cyanate. Recently Bahadur and coworkers[9,10] have observed that if under sterilized condition a mixture of paraformaldehyde, potassium nitrate, ferric chloride and water is exposed to artificial light, a number of aminoacids are synthesised in the mixture.

Formation of complex organic compounds by the action of high energy source like ultra-violet rays, X-rays and electric discharge on the mixture of simple gases like methane, ammonia, hydrogen and water, has been demonstrated by many workers like Horowitz and Miller[11], Miller and Urey[12], Lowe *et al*[13] and others[1,5].

It seems from the above summary, that the influence of phosphate and light on the formation of aminoacids has not been tackled and hence this study was undertaken. The interaction between NH_4NO_3 and KNO_3 and the energy material glucose in presence of titania, molybdic acid and vanadium pentoxide and phosphate has been investigated.

[331]

Experimental

Sterilized sets were used in these experiments. 10 ml of M/4 glucose and 10 ml. M/3 NH_4NO_3 or KNO_3 as required and 0·2 gm titania were taken in flasks 0·01 gm MoO_3 or V_2O_5 was added in one flask each and the mixture of two in two flasks. Two sets (one with $MoO_3+V_2O_5$ and one without it) were phosphated with 0·1 gm $CaHPO_4$. $2H_2O$. All sets were in duplicate. One set was exposed to 500 watt electric bulb, the other set kept covered with thick black cloth. The contents of the flasks were analysed for amino acids after definite intervals of time. The qualitative estimations were made by paper chromatography[16] and quantitative estimations by colorimetric method of Harding and Mclean[17].

The following abbreviations for the aminoacids have been used in the result recorded.

Gly for Glycine, Al for Alanine, Val for Valine, Leu for Leucine, Asp for Aspartic acid and Ly for Lysine.

TABLE 1

10 ml. M/4 glucose + 10 ml. M/3 NH_4NO_3 + 0·2 gm. TiO_2.   *Sterile*

Period of exposure in days	Aminoacids detected chromato-graphically	Amount of aminoacids with respect to glycine in gm/litre	Aminoacids detected chromato-graphically	Amount of aminoacids with respect to glycine in gm/litre
	Light		*Dark*	
1.	Gly., Val.	0·0248	...	...
2.	Gly., Val., Al.	0·0463	...	...
3.	Gly., Val., Al.	0·0783	Gly. faint ring.	traces
4.	Gly., Al.	0·0496	..	...
5.	Gly.	0·0318	...	...

TABLE 2

10 ml. M/4 glucose + 10 ml. M/3 NH_3NO_3 + 0·2 gm. TiO_2 + 0·1 gm. $CaHPO_4 2H_2O$

1.	Gly., Val.	0·0374	...	...
2.	Gly., Val., Al., Asp.	0·0689	Gly. (faint).	traces
3.	Gly., Val., Al., Leu., Asp.	0·1034	Gly., Al. (faint)	traces
4.	Val., Al., Leu.	0·0837	...	...
5.	Val., Al.	0·0398	...	...

TABLE 3

10 ml. M/4 glucose + 10 ml. M/3 NH_4HO_3 + 0·2 gm. TiO_2 + 0·01 gm. MoO_3

1.	Gly., Val.	0·0262	...	...
2.	Gly., Val., Al.	0·0498	...	...
3.	Gly., Val., Al., Asp. (faint)	0·0796	Gly. (faint)	traces
4.	Gly., Al.	0·0532	...	...
5.	Gly., Al.	0·0386	...	...

TABLE 4

10 ml. M/4 glucose + 10 ml. M/3 NH_4NO_3 + 0·2 gm. TiO_2 + 0·01 gm. V_2O_5

Sterile

Period of exposure in days	Aminoacids detected chromato-graphically	Amount of aminoacids with respect to glycine in gm/litre	Aminoacids detected chromato-graphically	Amount of aminoacids with respect to glycine in gm/litre
	Light		*Dark*	
1.	Gly., Val.	0·0251	...	...
2.	Gly., Val., Al.	0·0476	...	...
3.	Gly., Val., Al.	0·0784	Gly. (faint)	traces
4.	Gly., Val.	0·0498	...	...
5.	Gly., Val.	0·0363	...	...

TABLE 5

10 ml. M/4 glucose + 10 ml. M/3 NH_4NO_3 + 0·2 gm. TiO_2 + 0·02 gm. $(MoO_3 + V_2O_5)$ + 0·1 gm. $CaHPO_4\ 2H_2O$

1.	Gly., Val.	0·0596	...	...
2.	Gly., Val., Al.	0.0728	Gly. (faint)	traces
3.	Gly., Val., Al., Asp., Leu. (faint)	0·1058	Gly., Al.	traces
4.	Gly., Val., Al.	0·0937	Al. (faint)	traces
5.	Gly., Al.	0·0618	...	...

TABLE 6

10 ml. M/4 glucose + 10 ml. M/3 NH_4NO_3 + 0·2 gm. TiO_2 + 0·02 gm. $M_3O_3 + V_2O_5$

1.	Gly., Val., Al.	0·0281	...	...
2.	Gly., Val., Al., Asp.	0·0509	Gly.	traces
3.	Gly., Val., Al., Asp., Leu., Ly.	0·0862	Gly.	traces
4.	Gly., Aly., Leu., Ly.	0·0631	...	...
5.	Al., Leu.	0·0435	...	...

TABLE 7

10 ml. M/4 glucose + 10 ml. M/3 KNO_3 + 0·2 gm. TiO_2

1.	...	traces	...	...
2.	Gly., Val.	0·0412	...	...
3.	Gly., Val.	0·0623	Gly. (faint)	traces
4.	Aly., Val.	0·0481	...	...
5.	Al.	0·0286	...	...

TABLE 8

10 ml. M/4 glucose + 10 ml. M/3 KNO_3 + 0·2 gm. TiO_2 + 0·1 gm. $CaHPO_4.2H_2O$

Sterile

Period of exposure in days	Aminoacids detected chromatographically	Amount of aminoacids with respect to glycine in gm/litre	Aminoacids detected chromaographically	Amount of aminoacid with respect to glycine in gm/litr
	Light		*Dark*	
1.	Gly., Val.	0·0241	...	...
2.	Gly., Val., Al.	0·0583	Gly.	traces
3.	Gly., Val., Al., Asp.	0·0976	Gly. Al. (faint)	traces
4.	Gly., Al., Val, Asp.	0·0768	...	...
5.	Gly., Al., Val.	0·0589	...	...

TABLE 9

10 ml. M/4 glucose + 10 ml. M/3 KNO_3 + 0·2 gm. TiO_2 + 0·01 gm. MoO_3

1.	...	traces	...	...
2.	Gly., Val.	0·0442	...	...
3.	Gly., Val., Al.	0·0688	Gly.	traces
4.	Gly., Val.	0·0532	...	...
5.	Gly., Val.	0·0312	...	...

TABLE 10

10 ml. M/4 glucose + 10 ml. M/3 KNO_3 + 0·2 gm. TiO_2 + 0·01 mg. V_2O_5

1.	...	trac·s	...	...
2.	Gly., Val., Al.	0·0429		...
3.	Gly., Val., Al.	0·0679	Gly.	traces
4.	Gly., Val.	0·0517	...	...
5.	Val.	0·0298	...	...

TABLE 11

10 ml. M/4 glucose + 10 ml. M/3 KNO_3 + 0·2 gm. TiO_2 + 0·02 gm. (MoO_3 + V_2O_5)

1.	Gly., Val.	0·0207	..	...
2.	Gly., Val.	0·0468	Gly.	traces
3.	Gly., Val., Al.	0·0738	Gly., Al.	traces
4.	Gly., Val., Al.	0·0561	...	...
5.	Al., Val.	0·0341	...	..

TABLE 12

10 ml. M/4 glucose + 10 ml. M/3 KNO_3 + 0·2 gm. TiO_2 + 0·02 gm.
$(MoO_3 + V_2O_5)$ + 0·1 gm. $CaPHO_4$. $2H_2O$

Sterile

Period of exposure in days	Aminoacids detected chromatographically	Amount of aminoacids with respect to glycine in gm/litre	Aminoacids detected chromatographically	Amount of aminoacid with respect to glycine in gm/litre
	Light		*Dark*	
1.	Gly., Val., Al.	0·0263	...	...
2.	Gly., Val., Al., Asp.	0·0617	Gly.	traces
3.	Gly., Val., Al., Asp., Ly.	0·0998	Gly. Al.	traces
4.	Gly., Val., Al.	0·0781	Gly., Al.	traces
5.	Gly., Val.	0·0413	...	...

Discussion

A perusal of the experimental results (table 1·12) shows that when the systems consisting of NH_4NO_3 or KNO_3 and glucose are exposed to light in presence of titania and other photocatalysts MoO_3 or V_2O_5, an appreciable amounts of aminoacids are formed. The quantity as well as the number of aminoacids produced increases when the systems are phosphated with dicalcium phosphate. It supports the view point that phosphates form stable complexes with proteins and aminoacids both in soils and plants tissue as well as in vitro, thus making the protein or aminoacids molecules much more stable towards decomposition. Recently Dhar and Ghosh[18] from a study of the physical properties have established the possibility of the formation of phosphorylated compounds in vitro when phosphoric acid is mixed with aminoacids adenine and adenosine etc.

It is observed that systems containing molybdic acid give better results than those containing vanadium pentoxide and the mixture of these two photocatalysts give an appreciable increase which is more pronounced when the systems is phosphated. This may be probably due to the difference that molybdic acid is a bitter photocatalyst than vanadium pentoxide.

Furthermore, it is clear that the synthesis of aminoacids in the above sterile sets is highly facilitated by the absorption of light. In all the cases, the amounts of aminoacids formed are much higher than in the dark. In the exposed sets it seems that the energy liberated by the oxidation of the energy material as well as the energy absorbed in the form of light are utilized in the formation of aminoacids. But in the covered sets, only small amounts of aminoacids are synthesized because only the thermochemical energy due to the oxidation of the organic compounds are available.

In all the systems it is observed that there is an increase in the amount of aminoacids synthesized in the beginning which is followed by a decrease on prolonged exposure. It seems that along with photosynthesis of amino acids, photolysis is also taking place. Vaidyanathan *et al*[19], Dhar and Rao[20] and Nikolaev and Agapova[21] have also observed the photolysis of amino acids in presence of sensitizers.

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Formation of Aminoacids and changes during Nitrogen fixation

By

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Abstract

The soil organic nitrogen is mostly of protein nature and the major source of soil nitrogen is the organic matter, which in addition to the nitrogen present in it, also fixes atmospheric nitrogen, while undergoing slow oxidation at the soil surface, increasing the aminoacids content. The amount and number of aminoacids are greater in phosphated system than unphosphated.

Introduction

Aminoacids are the building units of the proteins of all the living matter on the earth and their formation in nature has drawn the attention of scientists. Aminoacids exist in free state in many soils. Free aminoacids are of potential importance both to microbial nutrition and plant life[1,2,3]. Dadd *et al*[4] examined nine soils and obtained ninhydrin spots for all soil extracts. Biswas and Das[5] detected free aminoacids like aspartic acid, glutamic acids, leucine, valine, cystine and alanine in aqueous alcoholic leachates in soils. Simonart and Peeters[6] extracted forest soils, leaf mould and green house soil samples with 70% ethanol and chromatographed the concentrated extract on paper.

Recently Payne *et al*[7] noted that aqueous soils extracts concentrated by freeze drying yielded ninhydrin positive spots on paper. Isolation of aminoacids in acid hydrolysates of soils by Suzuki[8], Schreiner and Shorey[9] Robinson[10], Kivekas[11] and Kojima[12] have come to the conclusion that the soil organic nitrogen is mostly of protein nature. Bremner[13] could detect as many as 21 aminoacids in acid hydrolytates of some U. K. soils and reported a recovery of 33% to 37% of the organic nitrogen as amino nitrogen in the soil he examined.

Dhar and Roy[14] have also shown the formation of aminoncids by exposing normal solutions of nitrates and glucose with titania as photosensitiser. Similar studies have been reported on Canadian soils by Parkar *et al*[15], on Podzol and Praire soils by Davidson *et al*[16] and on French African soils by Carles *et al*[17] and Carles and Decau[18].

Barnes[19] from the Woburn Experimental Station has reported an increase in the nitrogen content with straw undergoing oxidation. Bjälfve[20] in Sweden has also observed that straw when ploughed in fixes atmospheric nitrogen and also that light markedly increases the fixation of nitrogen by the slow oxidation of straw in soil. Hutchinson[21] and Jensen[22] fixed nitrogen under laboratory conditions mixing soil and straw. Similarly Barbier and Boischot[23] and Boischot[24] report that incorporation of straw with soil maintained or increased the nitrogen status of the soil even after continuous cropping.

In order to throw further light on this important problem, it was thought necessary to obtain some quantitative results. The influence of wheat straw, peat

ahd saw dust and basic slags on aminoacids formation and changes during nitrogen fixation has been investigated and reported in this paper.

Experimental

The experiments were carried out with Sheila Dhar Institute lawn soil. All the ingredients *viz.* soil, phosphate, wheat straw, sawdust and peat used in the experiments were sieved to 100 mesh.

200 gms. of soil were taken in wide mouth bottles (1 lb. cap). To this the required carbonaceous materials and phosphates were introduced as 1% carbon and 0.5% P_2O_5 respectively on an oven dry basis and the contents were thoroughly mixed in a big pestle and mortar and the whole mixture was made as uniform as possible. Two similar sets were arranged side by side, one of which was exposed to light and other was covered with a thick black cloth. In all the bottles the moisture content was maintained at 40 percent level throughout the experiment. The contents of the bottles were stirred daily with the help of glass rod. At regular intervals of time, composite samples were taken out from all the bottles and were analysed for total carbon, total nitrogen and aminoacids. The qualitative estimation of aminoacids was done by two dimensional chromatography and quantitative by Harding and Mclean method[25].

The following abbreviations for the aminoacids studied have been used.

Al. for Alanine   Glu. for Glutamic acid
Va. for Valine   Ly. for Lysine
Asp. for Aspartic acid   Ar. for Arginine
Leu. for Leucine   Hi. for Histidine
Gly. for Glycine

T.B.S. for Tata Basic Slag
G.B.S. for German Basic Slag.

The experimental observations are recorded in the following pages.

Discussion

From the experimental results recorded in the foregoing pages, it is observed that there is an appreciable oxidation of carbon from soil sets mixed with wheat-straw, peat and sawdust, more in light than in dark. There is concomitant increase in nitrogen along with carbon oxidation. The amount of carbon oxidised as well as an increase in the nitrogen fixed are in the following order wheatstraw> peat> sawdust.

It is interesting to note that along with nitrogen fixation, the number and amount of aminoacids formed is alway greater in the sets exposed to light than in those kept in the dark. These observations show that light energy is helpful in nitrogen fixation and subsequent utlization of fixed nitrogen in the synthesis of aminoacids. It is interesting to note that Tata and German basic slags favour the formation of histidine, which is in agreement with the observations of Rishi[26].

In explaining the photosynthesis in plants Dhar postulated that the important photochemical reaction was the decomposition of water by the absorption of light. Also in explaining the nitrogen fixation the best mechanism seems to be the same *i.e.* the decomposition of water into H and OH by the absorption of energy obtained from the oxidation of carbohydrates like cellulose, lignin and fat etc. Moreover in the presence of light, the light energy whether from sun or from an artificial source, is absorbed by the system and utilized in increasing the nitrogen fixation.

$$H_2O + 112 \text{ K Cal.} = H + OH$$
$$6H + N_2 = 2NH_3$$
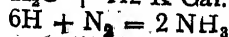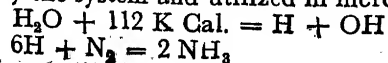
The ammonia formed readily undergoes oxidation and forms nitrite, nitrate which finally forms aminoacids and proteins in the soil.

$$NH_3 \xrightarrow{+ O_2} NO_2 \xrightarrow{+ O_2} NO_3 \xrightarrow{+ \text{ carbohydrate}} \text{Aminoacids} \longrightarrow \text{Proteins}$$
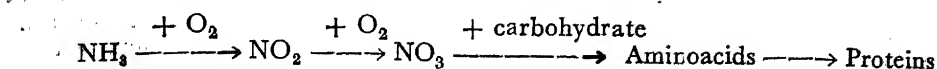
Dhar and coworkers[27,28,24] have shown that in soils the process of nitrogen fixation is always opposed by ammonification and nitrification. Thus on one hand, nitrogen fixed on the surface of soil undergoes various changes aided by light absorption to form aminoacids and proteins and on the other hand, these aminoacids and proteins formed in the soil undergo ammonification and nitrification which are accelerated by light absorption and form nitrite and nitrate. In these series of reaction the unstable ammonium nitrite is formed which undergoes decomposition liberating energy and nitrogen gas as in the following equation :

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O + 718 \text{ K Cal.}$$
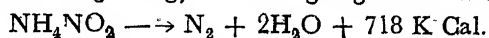
But the addition of phosphate *i.e.* Tata or German Basic Slags to the systems, form stable phosphoproteins or phospho-ligno-proteins and resist the ammonification and nitrification processes. It is clear from the results that the amount and number of aminoacids is greater in phosphated systems than unphosphated one, which is in agreement with the observations of Dhar and Roy[14].

It is therefore, concluded from our investigations that the soil organic nitrogen is mostly of protein nature and the major source of soil nitrogen is the organic matter, which in addition to the nitrogen present in it, also fixes atmospheric nitrogen, while undergoing slow oxidation at the soil surface, increasing the aminoacids contents.

TABLE 1

Av. temp. 29°C   200 gms. soil

Period of exposure in days	Total carbon gm.	Total Nitrogen gm.	Amino acids identified chromato-graphically	Amount of amino acids with respect to glycine (mgm.)
			Light	
0	1·4252	0·1396	Al., Va., Glu.	...
60	1·3527	0·1405	Al., Va., Glu.	...
120	1·3218	0·1408	Al., Va., Glu., Ly.	0·0309
180	1·2757	0·1412	Al., Va., Glu., Ly., Ar.	0·0348
240	1·2042	0·1417	Al., Va., Glu., Ly., Ar.	0·0334
			Dark	
0	1·4252	0·13960	Al., Va., Glu.	...
60	1·3765	0·14000	Al., Va., Glu.	...
120	1·3490	0·14021	Al., Va., Glu.	...
180	1·3186	0·14040	Al., Va., Glu., Ly.	0·0271
240	1·2864	0·14060	Al., Va., Glu., Ly.	0·0276

TABLE 2

Av. temp. 29°C.   *200 gms Soil + 1% C as Wheat straw*

Period of exposure in days	Total carbon gm.	Total Nitrogen gm.	Amino acids identified chromato-graphically	Amount of amino acids with respect to glycine (mgm)
			Light	
0	3·4252	0·1729	Al., Va., Glu.	...
60	3·0584	0·1833	Al., Va., Glu, Leu.	1·7964
120	2·8530	0·1887	Al., Glu., Va., Leu., Asp.	2·4632
180	2·6779	0·1935	Al., Va., Glu., Asp., Leu., Ar.	2·7289
240	2·4709	0·1926	Al., Va., Glu., Ap.	2·6437
			Dark	
0	3·4252	0·1729	Al., Glu., Va.	...
60	3·1404	0·1774	Al., Glu., Va.	1·0721
120	2·9837	0·1797	Al., Glu., Va., Leu.	1·4893
180	2·8139	0·1821	Al., Glu., Va., Leu., Asp.	1·9817
240	2·6415	0·1818	Al., Glu., Va., Leu., Asp., Ar.	1·8763

TABLE 3

Av. temp. 29°C.   *200 gms. Soil + 1% C as Wheat straw + 0·5% P_2O_5 as Tata basic slag*

Period of exposure in days	Total carbon gm.	Total Nitrogen gm.	Amino acids identified chromato-graphically	Amount of amino acids with respect to glycine (mgm)
			Light	
0	3·4252	0·1729	Al., Va., Glu.	...
60	2·8628	0·1963	Al., Va., Glu., Leu.	2·5672
120	2·6685	0·2037	Al., Va., Glu., Leu., Asp.	3·7124
180	2·4005	0·2143	Al., Va., Glu., Leu., Asp., Ly., Hi, Ar.	4·4872
240	2·3013	0·2128	Al., Va., Glu., Leu., Asp., Ly., Hi., Ar.	4·2097
			Dark	
0	3·4252	0·1729	Al., Va., Glu.	...
60	3·0390	0·1830	Al., Glu., Va.	1·6698
120	2·8434	0·1877	Al., Glu., Va., Leu., Asp.	2·4367
180	2·6373	0·1911	Al., Glu., Va., Leu., Asp., Ar.	2·8189
240	2·4854	0·1907	Al., Glu., Va., Leu., Asp., Ar., Hi.	2·7496

TABLE 4

Av. temp. 29°C.   200 gms. Soil + 1% C as Wheat straw + 0·5% P_2O_5 as German basic slag

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Amino acids identified chromato-graphically	Amount of amino acids with glycine (mgm)
			Light	
0	3·4252	0·1729	Al., Glu., Va.	...
60	2·8340	0·1982	Al., Glu., Va., Leu.	2·7467
120	2·6559	0·2051	Al., Glu., Va., Leu., Asp.	3·8923
180	2·3974	0·2157	Al., Glu., Va., Leu., Asp., Ar., Hi.	4·5871
240	2·2784	0·2146	Al., Va., Glu., Leu., Asp., Ar., Hi.	4·4108
			Dark	
0	3·4252	0·1729	Al., Glu., Va.	...
60	3·0376	0·1831	Al., Va., Glu., Leu.	1·7224
120	2·8426	0·1877	Al., Va., Glu., Leu., Hi.	2·4178
180	2·6361	0·1913	Al., Va., Glu., Leu., Hi.	2·9119
240	2·4980	0·1904	Al., Va., Glu., Leu., Hi., Asp.	2·8274

TABLE 5

Av. temp. 29°C.   200 mgs. Soil + 1% C as Peat

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Amino acids identified chromato-graphically	Amount of amino acids with glycine (mgm)
			Light	
0	3·4252	0·2486	Al., Glu., Va.	...
60	3·2003	0·2548	Al., Glu., Va., Leu.	1·5678
120	3·0962	0·2577	Al., Gly., Va., Leu., Asp.	2·2221
180	2·9684	0·2612	Al., Gly., Va., Leu., Asp., Ar.	2·4678
240	2·8209	0·2608	Al., Glu., Va., Leu., Asp. Ar.	2·3291
			Dark	
0	3·4252	0·2486	Al., Glu. Va.	...
60	3·2338	0·2514	Al., Gly., Va., Leu.	0·9871
120	3·1396	0·2526	Al., Va., Gly., Asp., Leu.	1·2645
180	3·0502	0·2537	Al., Va., Gly., Asp., Leu.	1·4767
240	2·9588	0·2534	Al., Va., Gly., Asp., Ar.	1·3562

TABLE 6

Av. temp. 29°C.   *200 gms. Soil + 1% C as Peat + 0·5% P$_2$O$_5$ Tata basic slag*

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Amino acids identified chromato-graphically	Amount of amino acids with respect to glycine (mgm.)
			Light	
0	3·4252	0·2486	Al., Glu., Va.	...
60	3·1190	0·2607	Al., Glu. Va., Leu.	2·1976
120	2·9510	0·2673	Al., Glu., Va., Leu., Asp.	3·4018
180	2·7864	0·2723	Al., Glu., Va., Leu., Asp., Hi.	4·0862
240	2·6383	0·2714	Al., Va., Glu., Leu., Asp., Hi., Ar.	3·9621
			Dark	
0	3·4252	0·2486	Al., Glu., Va.	...
60	3·2049	0·2530	Al., Gly., Va.	1·2654
120	3·1035	0·2549	Al., Gly., Va., Leu.	1·8934
180	2·9968	0·2568	Al., Glu., Va., Leu.	2·4681
240	2·9315	0·2563	Al., Glu., Va., Leu., Asp., Hi.	2·3297

TABLE 7

Av. temp. 29°C.   200 gms. Soil + 1% C as Peat + 0·5% P$_2$O$_5$ as German basic slag

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Amino acids identified chromato-graphically	Amount of amino acids with respect to glycine (mgm.)
			Light	
0	3·4252	0·2486	Al., Glu., Va.	...
60	3·1155	0·2612	Al., Glu., Va., Gly.,	2·4347
120	2·9467	0·2680	Al., Glu., Va., Asp., Leu.	3·6129
180	2·7773	0·2741	Al., Glu., Va., Asp., Hi., Ar., Leu.	4·3627
240	2·6343	0·2732	Al., Glu., Va., Asp., Hi., Ar.	4·1267
			Dark	
0	3·4252	0·2486	Al., Glu., Va. (faint)	...
60	3·2023	0·2531	Al., Glu., Va.	1·8169
120	3·1006	0·2551	Al., Glu., Va., Leu.	2·4379
180	2·9943	0·2570	Al., Glu., Va., Leu., Asp.	2·8735
240	2·9270	0·2567	Al., Glu., Va., Leu., Ar., Asp.	2·8361

TABLE 8

Av. temp. 29°C.   *200 gms. Soil + 1% C as Sawdust*

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Amino acids identified chromatographically	Amount of amino acids with respect to glycine (mgm)
			Light	
0	3·4252	0·1702	Al., Gly.	...
60	3·2341	0·1751	Al., Gly., Va.	1·3469
120	3·1424	0·1774	Al , Glu., Va., Leu., Asp.	2·0546
180	3·0451	0·1797	Glu., Va., Asp., Ly., Ar.	2·2718
240	2·9410	0·1796	Va., Glu., Asp., Leu., Ly., Ar.	2·1864
			Dark	
0	3·4252	0·1702	Al., Glu.	...
60	3·2504	0 1725	Al., Gly., Va.	0·8634
120	3·1575	0·17.6	Al., Glu., Va., Leu.	1·1351
180	3·0681	0·1747	Al., Glu., Va., Leu., Asp.	1·2867
240	2·9823	0·1746	Va., Glu., Leu., Asp., Ar.	1·0359

TABLE 9

Av. temp. 29°C.   *200 gms. Soil + 1% C as Sawdust + 0·5% P_2O_5 as Tata basic slag*

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Amino acids identified chromatographically	Amount of amino acids with respect to glycine (mgm)
			Light	
0	3·4252	0·1702	Al., Glu., Va.	...
60	3·1250	0·1814	Al., Glu., Va., Leu.	1·9863
120	2·9934	0·1860	Gly., Va., Leu., Asp.,	3·1067
180	2·8309	0·1918	Va., Glu., Al., Ar., Hi., Asp.	3·8103
240	2·6888	0·1901	Va., Glu., Al., Asp., Ar., Hi., Ly.	3·4675
			Dark	
0	3·4252	0·1702	Al., Glu., Va.	...
60	3·2103	0·1744	Al., Glu., Va.,	1·0457
120	3·1065	0·1763	Al., Glu., Va., Ly.	1.5661
180	3·0166	0·1780	Al., Glu., Va., Asp.	2·1869
240	2·9476	0·1779	Al., Glu., Va., Asp., Hi., Ar., Ly.	2·0049

TABLE 10

Av. temp. 29°C.   *200 gms. Soil + 1% C as Sawdust + 0·5% P_2O_5 as German basic slag*

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Amino acids identified chromatographically	Amount of amino acids with respect to glycine (mgm)
			Light	
0	3·4252	0·1702	Al., Glu., Va.	...
60	3·1209	0·1818	Al., Gl., Va.	1·2672
120	2·9788	0·1864	Ly., Gly., Va., Asp.	3·3059
180	2·8159	0·1921	Hi., Glu., Va., Ly., Asp., Ar.	4·0547
240	2·6668	0·1914	Hi., Glu., Va., Ly., Leu., Asp.	2·8672
			Dark	
0	3·4252	0·1702	Al., Glu., Va.	...
60	3·2056	0·1745	Al., Glu., Va.,	1·3721
120	3·1034	0·1764	Ly., Gly., Va., Asp.	1·8729
180	3·0089	0·1782	Hi., Glu., Va., Asp., Ly.	2·3462
240	2·9315	0·1779	Al., Va., Glu., Hi., Asp., Ar.	2·1789

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Effect of Organic matter and algae on the availability of Phosphate and Nitrogen fixation

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Abstract

When carbonaceous materials are mixed with soil and allowed to undergo slow oxidation, there is an appreciable increase in nitrogen status of the soil, more in light than in dark. In the sets inoculated with blue green algae, Tolypothrix tenius and Anabaena naviculoides and green alga Chlorella vulgaris, there is small saving of carbon along with nitrogen fixation. Along with carbon oxidation there is concomitant increase in the availability of phosphate and nitrogen fixation.

Introduction

The origin of soil nitrogen has been highly controversial. A huge amount of nitrogen is removed from the arable lands every year through various processes such as harvest of crops, erosion, leaching and loss as elementry nitrogen from the soil surface[1,2]. It is obvious therefore that inorder to maintain their fertility soils must have some mechanism by which they are able to fix nitrogen from some source and thus make up for the loss totally or partially. Various scientists have suggested different mechanisms to explain nitrogen fixation in soils.

A considerable amount of work has been carried on recently on the part played by blue green algae in fixing atmospheric nitrogen, especially in paddy fields. De[3], Watanabe[4], Allen[5], Okuda and Yamaguchi[6] have reported considerable increase in the yield of paddy crop by the application of blue green algae.

According to Pearsall[7] the blue green algae are frequently met in abundance in fresh water specially in neutral and alkaline waters with a relatively high content of dissolved organic matter and a low content of nitrate. These observations show that blue green algae can grow better provided a sufficient amount of organic matter is already present in the soil.

On the other hand, Uppal, Patel and Daji[8] have shown that Azotobacter plays an important role in the nitrogen recuperation of soils at Karjat (India). Russell[9] has stated. "There is no evidence yet that algae play any important role in enriching the soils of temperate regions with nitrogen, although species belonging to the genera containing nitrogen fixing forms are fairly widespread".

Hence in order to throw light on this problem, it was thought necessary to study quantitatively the part played by the algae in enriching out soils and on the availability of phosphate in presence and absence of different organic materials has been taken.

Experimental

The experiments were carried out with the Sheila Dhar Institute lawn soil. All the ingredients *viz* :- soil, carbonaceous matter wheat straw and peat used in these experiments were sieved to 100 mesh.

200 gms of the soil were taken in wide mouth bottles (1 lb. capacity). To this required carbonaceous materials were introduced as 1% carbon on an oven dry basis and the whole mixture was made uniform. Then, wherever required the soil in the bottles was inoculated with Anabaena naviculoides, Tolypothrix tenuis and Chlorella vulgaris. Two similar sets were arranged side by side, one of which was exposed to light and the other was covered with a thick black cloth. In all the bottles the moisture content was maintained at 40% level throughout the experiment. The contents of the bottles were stirred daily with the help of a glass rod. At regular intervals of time, composite samples were taken out from all the sets and were analysed for total carbon, nitrogen and available phosphate by A. O. A. C. methods.

Bacteria free Unialgal cultures of the above three algae were obtained from Dr. A. K. Mitra, an eminent algologist, University of Allahabad India. Stock cultures of these algae were then prepared by growing them in the following media

Media for Anabaena and Tolypothrix			Media for Chlorella		
KNO_3	...	0·2 gm.	NH_4NO_3	...	0·2 gm.
K_2HPO_4	...	0·2 gm.	K_2HPO_4	...	0·2 gm.
$MgSO_4\, 7H_2O$	...	0·2 gm.	$MgSO_4\, 7H_2O$	..	0·2 gm.
$CaCl_2$	..	0·1 gm.	$CaCl_2$	...	0·1 gm.
$FeCl_3\ 1\%$	...	2 drops	$FeCl_3\ 1\%$	...	2 drops
Pyrex distilled water		1000 c.c	Pyrex distilled water	...	1000 c.c

TABLE 1

Av. Temp. 29°C 200 *gm. Soil*

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Efficiency	Avl. P_2O_5 gm.
		Light		
0	1·4252	0·1398	...	0·0272
60	1·3527	0·1405	12·4	0·0302
120	1·3218	0·1408	11·6	0·0318
180	1·2757	0·1412	10·7	0·0338
240	1·2042	0·1417	9·5	0·0354
		Dark		
0	1·4252	0·13960	...	0·0272
60	1·3765	0·14000	8·2	0·0288
120	1·3490	0·14021	8·0	0·0306
180	1·3186	0·14040	7·5	0·0313
240	1·2864	0·14050	...	0·0328

TABLE 2

200 gm. Soil + Chlorella vulgaris

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Efficiency	Avl. P_2O_5 gm.
		Light		
0	1·4252	0·1396	...	0·0272
60	1·3760	0·1406	20·3	0·0307
120	1·3512	0·1410	18·9	0·0323
180	1·3142	0·1414	16·2	0·0339
240	1·2778	0·1419	15·6	0·0358
		Dark		
0	1·4252	0·1396	...	0·0272
60	1·3763	0·1400	8·1	0·0289
120	1·3489	0·1402	7·8	0·0308
180	1·3183	0·1404	7·4	0·0314
240	1·2863	0·1406	...	0·0329

TABLE 3

200 gms. Soil + Anabaena naviculoides

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Efficiency	Avl. P_2O_5 gm.
		Light		
0	1·4252	0·1396	...	0·0272
60	1·3728	0·1411	28·6	0 0306
120	1·3488	0·1416	26·1	0·0319
180	1·3114	0·1422	22·9	0·0336
240	1·2771	0·1424	18·9	0·0357
		Dark		
0	1·4252	0·13960	...	0·0272
60	1·3761	0·14002	8·5	0·0289
120	1·3490	0·14019	7·7	0·0306
180	1·3179	0·14042	7·6	0·0314
240	1·2856	0·14063	7·3	0·0328

TABLE 4

200 gms. Soil + Tolypothrix tenuis

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Efficiency	Avl. P_2O_5 gm.
		Light		
0	1·4252	0·1396	...	0·0272
60	1·3736	0·1412	31·0	0·0307
120	1·3504	0·1417	28·0	0·0321
180	1·3126	0·1423	23·0	0·0337
240	1·2776	0·1425	19·6	0·0356
		Dark		
0	1·4252	0.13960	...	0·0272
60	1·3755	0·14003	8·4	0·0289
120	1·3490	0·14019	7·7	0·0307
180	1·3180	0·14042	7·6	0·0314
240	1·2854	0·14062	7·2	0·0328

TABLE 5

Av. Temp. 29°C — 200 gms. Soil + 1% C as Wheat straw

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Efficiency	Avl. P_2O_5 gm.
Light				
0	3·4252	0·1729	...	0·0272
60	3·0584	0·1833	28·3	0·0347
120	2·8530	0·1887	27·6	0·0398
180	2·6779	0·1935	27·5	0·0443
240	2·4709	0·1926	27·3	0·0479
Dark				
0	3·4252	0·1729	...	0·0272
60	3·1404	0·1774	15·8	0·0224
120	2·9837	0·1797	15·4	0·0365
180	2·8139	0·1821	15·3	0·0408
240	2·6415	0·1818	...	0·0430

TABLE 6

200 gms. Soil + 1% C as Wheat straw + *Anabaena*

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Efficiency	Avl. P_2O_5 gm.
Light				
0	3·4252	0·1729	...	0·0272
60	3·1385	0·1860	45·6	0·0348
120	2·9841	0·1923	43·9	0·0401
180	2·8063	0·1998	43·4	0·0445
240	2·6188	0·1986	42·2	0·0479
Dark				
0	3·4252	0·1729	...	0·0272
60	3·1403	0·1774	15·8	0·0324
120	2·9838	0·1797	15·4	0·0366
180	2·8139	0·1821	15·3	0·0407
240	2·6416	0·1819	...	0·0431

TABLE 7

200 gms. Soil + 1% C as Wheat straw + *Chlorella*

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Efficiency	Avl. P_2O_5 gm.
Light				
0	3·4252	0·1729	...	0·0272
60	3·1412	0·1835	37·3	0·0351
120	2·9852	0·1891	36·5	0·0402
180	2·8074	0·1939	33·9	0·0447
240	2·6199	0·1923	32·7	0·0481
Dark				
0	3·4252	0·1729	...	0·0272
60	3·1405	0·1774	15·8	0·0325
120	2·9836	0·1797	15·4	0·0365
180	2·8140	0·1821	15·3	0·0409
240	2·6414	0·1819	...	0·0431

TABLE 8

Av. Temp. 29°C   *200 gms. Soil + 1% C as Wheat straw + Tolypothrix*

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Efficiency	Avl. P_2O_5 gm.
		Light		
0	3·4252	0·1729	...	0·0272
60	3·1398	0·1867	48·3	0·0350
120	2·9845	0·1935	46·7	0·0399
180	2·8069	0·2017	46·5	0·0449
240	2·6196	0·2008	...	0·0479
		Dark		
0	3·4252	0·1729	...	0·0272
60	2·1404	0·1774	15·8	0·0326
120	2·9836	0·1797	15·4	0·0364
180	2·8140	0·1821	15·3	0·0408
240	2·6416	0·1820	..	0·0430

TABLE 9

200 gms. Soil + 1% C as Wheat straw + 0·5% P_2O_5 as Tata basic slag

		Light		
0	3·4252	0·1729	...	0·5760
60	2·8628	0·1963	41·6	0·6198
120	2·6685	0·2037	40·7	0·6447
180	2·4005	0·2143	40·4	0·6753
240	2·3013	0·2128	...	0·6941
		Dark		
0	3·4252	0·1729	...	0·5760
60	3·0390	0·1830	26·1	0·6119
120	2·8434	0·1877	25·4	0·6387
180	2·6373	0·1911	23·00	0·6558
240	2·4854	0·1907	...	0·6789

TABLE 10

200 gms. Soil + 1% C as Wheat straw + 0·5% P_2O_5 as T.B.S. + Chlorella

		Light		
0	3·4252	0·1729	...	0·5760
60	2·9684	0·1970	52·7	0·6213
120	2·7160	0·2092	51·1	0·6474
180	2·5374	0·2182	51·0	0·6781
240	2·4173	0·2169	...	0·6987
		Dark		
0	3·4252	0·1729	...	0·5760
60	3·3904	0·1830	26·1	0·6118
120	2·84343	0·1877	25·4	0·6386
180	2·63732	0·1911	23·0	0·6561
240	2·48547	0·1902	...	0·6787

TABLE 11

Av. Temp. 29°C   200 *gms. Soil* + 1% *C as Wheat straw* + 0·5%
P_2O_5 *as T.B.S.* + *Anabaena*

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Efficiency	Avl. P_2O_5 gm.
Light				
0	3·4252	0·1729	..	0·5760
60	2·9604	0·1985	55·0	0·6209
120	2·7152	0·2110	53·6	0·6467
180	2·5356	0·2191	51·9	0·6769
240	2·3866	0·2183	...	0·6979
Dark				
0	2·4252	0·1729	...	0·5760
60	2·0392	0·1830	26·1	0·6116
120	2·84343	0·1877	25·4	0·6387
180	2·63738	0·1911	23·0	0·6559
240	2·48541	0·1907	...	0·6788

TABLE 12

200 *.gm. Soil* + 1% *C as Wheat straw* + 0·5 P_2O_5 *as T.B.S.* + *Tolypothrix*

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Efficiency	Avl. P_2O_5 gm.
Light				
0	3·4252	0·1729	...	0·5760
60	2·9629	0·1992	56·8	0·6210
120	2·7159	0·2115	54·4	0·6469
180	2·5366	0·2200	53·0	0·6769
240	2·3580	0·2194	...	0·6983
Dark				
0	3·4252	0·1729		0·5760
60	2·0392	0·1830	26·1	0·6117
120	2·8434	0·1877	25·4	0·6387
180	2·63736	0·1911	23·0	0·6558
240	2·4854	0·1907	...	0·6787

TABLE 13

200 *gms. Soil* + 1% *C as Peat*

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Efficiency	Avl. P_2O_5 gm.
Light				
0	3·4252	0·2486	...	0·0272
60	3·2003	0·2548	27·5	0·0338
120	3·0952	0·2577	27·6	0·0384
180	2·9684	0·2612	27·5	0·0429
240	2·8309	0·2608	...	0·0467
Dark				
0	3·4252	0·2486	...	0·0272
60	3·2338	0·2514	14·1	0·0319
120	3·1396	0·2526	14·0	0·0359
180	3·0502	0·2537	13·6	0·0397
240	2·9538	0·2534	...	0·0·423

TABLE 14

Av. Temp. 29°C   200 *gms. Soil* + 1% *C as Peat* + *Chlorella*

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Efficiency	Avl. P_2O_5 gm.
		Light		
0	3·4252	0·2486		0·0272
60	3·2114	0·2551	31·8	0·0341
120	3·1054	0·2581	29·7	0·0388
180	2·9885	0·2615	29·5	0·0431
240	2·8634	0·2609	...	0·0469
		Dark		
0	3·4252	0·2696	...	0·0272
60	3·2337	0·2514	14·1	0·0320
120	3·1397	0·2526	14·0	0·0358
180	3·0501	0·2537	13·6	0·0398
240	2·9537	0·2535	...	0·0423

TABLE 15

200 *gms. Soil* + 1% *C as Peat* + *Anabaena*

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Efficiency	Avl. P_2O_5 gm.
		Light		
0	3·4252	0·2486	...	0·0272
60	3·2203	0·2554	33·1	0·0339
120	3·1031	0·2587	33·1	0·0385
180	2·9860	0·2622	30·9	0·0429
240	2·8579	0·2618	...	0·0467
		Dark		
0	3·4252	0·2486	...	0·0272
60	3·2338	0·2514	14·1	0·0319
120	3·1396	0·2526	14·0	0·0359
180	3·0501	0·2537	13·6	0·0397
240	2·9538	0·2536	...	0·0422

TABLE 16

300 *gms. Soil* + 1% *C as Peat* + *Tolypothrix*

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Efficiency	Avl. P_2O_5 gm.
		Light		
0	3·4252	0·2486	...	0·0272
60	3·2210	0·2556	34·2	0·0340
120	3·1039	0·2589	32·0	0·0387
180	2·9877	0·2625	31·7	0·0429
240	2·8610	0·2620	...	0·0468
		Dark		
0	3·4252	0·2486	...	0·0272
60	3·2337	0·2514	14·1	0·0319
120	3·1397	0·2526	14·0	0·0358
180	3·0500	0·2537	13·6	0·0399
240	2·9536	0·2534		0·0422

TABLE 17

Av. Temp. 29°C   200 *gms. Soil* + 1% *C as Peat* + 0·5% P_2O_5 *as*
Tata basic slag

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Efficiency	Avl. P_2O_5 gm.
	Light			
0	3·4252	0·2486	...	0·5760
60	3·1190	0·2607	39·5	0·6132
120	2·9510	0·2673	39·4	0·6397
180	2·7864	0·2723	37·1	0·6622
240	2·6383	0·2714	...	0·6814
	Dark			
0	3·4252	0·2486	...	0·5760
60	3·2049	0·2530	19·9	0·6082
120	3·1035	0·2549	19·3	0·6246
180	2·9968	0·2568	19·1	0·6478
240	2·9315	0·2563	...	0·6603

TABLE 18

200 *gms. Soil* + 1% *C as Peat* + 0·5% P_2O_5 *as T.B.S.* + *Chlorella*

	Light			
0	3·4252	0·2486	...	0·5760
60	3·1371	0·2610	43·0	0·6136
120	2·9834	0·2675	42·7	0·6399
180	2·8366	0·2725	40·6	0·6626
240	2·6901	0·2720	...	0·6819
	Dark			
0	3·4252	0·2486	...	0·5760
60	3·20496	0·2530	19·9	0·6083
120	3·1036	0·2549	19·3	0·6247
180	2·99684	0·2568	19·1	0·6479
240	2·93151	0·2563	...	0·6602

TABLE 19

200 *gms. Soil* + 1% *C as Peat* + 0·5% P_2O_5 *as T.B.S.* + *Anabaena*

	Light			
0	3·4252	0·2486	...	0·5760
60	3·1338	0·2615	44·2	0·6134
120	2·9805	0·2680	43·6	0·6397
180	2·8333	0·2732	41·5	0·6623
240	2·6880	0·2724	...	0·6816
	Dark			
0	3·4252	0·2486	...	0·5760
60	3·2049	0·2530	19·9	0·6082
120	3·10352	0.2549	19·3	0·6246
180	2·9968	0·2568	19·1	0·6779
240	2·93153	0·2563	...	0·6604

TABLE 20

200 gms. Soil + 1% C as Peat + 0·5% P_2O_5 as T.B.S. + Tolypothrix

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Efficiency	Avl P_2O_5 gm.
		Light		
0	3·4252	0·2486	...	0·5760
60	3·1351	0·2620	46·1	0·6135
120	2·9814	0·2689	45·7	0·6399
180	2·8343	0·2748	44·3	0·6625
240	2·6884	0·2741	...	0·6818
		Dark		
0	3·4252	0·2486	...	0·5760
60	3·20494	0·2530	19·9	0·6083
120	3·1036	0·2549	19·3	0·6247
180	2·9968	0·2568	19·1	0·6478
240	2·9315	0·2563	...	0·6604

Discussion

From the experimental results recorded in the foregoing pages it appears that when carbonaceous matter wheat straw and peat are mixed with soil and allow d to undergo slow oxidation in air, there is an appreciable increase in the nitrogen content and available phosphate of the soil. Both oxidation of carbon, fixation of nitrogen and availability of phosphate are enhanced by the addition of Tata basic slag and always found to be greater in light than in dark. In these experiments the solvent action of organic matter seems to be chiefly due to the production of carbonic and organic acids formed during the oxidation and decomposition of organic substances. Small quantities of nitrous and nitric acids formed during the ammonification and nitrification of nitrogenous compounds may also favour this reaction.

$$Ca_3(PO_4)_2 + 2H_2CO_3 = 2 CaHPO_4 + Ca (HCO_3)_2$$
$$Ca_3 (PO_4)_2 + 4HNO_3 = 2 Ca (NO_3)_2 + Ca (H_2PO_4)_2$$
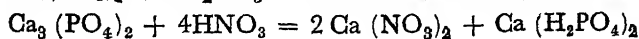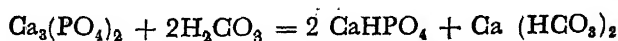
The first dissociation constants of citric, tartaric, oxalic, acetic and butyric acids are much higher than the second and third dissociation constants of phosphoric acid and these acids can easily convert the triortho salts of alkaline earth phosphates into di- and mono- phosphates. As regards carbonic acid, its first and second dissociation constants are much higher than the third dissociation constant of phosphoric acid, carbonic acid converts the tricalcium phosphate into dicalcium phosphate which is more soluble than tricalcium phosphate. Thus the availability of phosphate is increased in the soil rich in carbonic acid obtained from the oxidation of organic substances.

Dhar[10] has shown that when carbonic acid is passed through a suspension of basic slag, rock phosphate, tricalcium phosphate and dicalcium phosphate the amount of P_2O_5 passing into solution increases. Struthers and Sieling [11], Bradley and Sieling[12] and Swenson, Cole and Sieling[13] have assigned a

specific role to organic matter in making phosphates more readily available. Dean and Robins [4], Kurtz *et al*[15] and others[16,17,18] have observed that certain organic ions are effective in extracting phosphate from soil.

Furthermore, the experimental results show that the efficiency of nitrogen fixation, which is defined as the number of milligrams of nitrogen fixed per gram of carbon oxidised, is always found to be greater in sets inoculated with algae than those without it. With Anabaena and Tolypothrix the efficiency is always found to be greater than that with Chlorella. This is because along with carbon saving, both Anabaena and Tolypothrix being nitrogen fixers, are able to increase the nitrogen content of the system, thus giving a higher efficiency.

In the sets inoculated with algae, some saving of carbon and a small increase in nitrogen was always found in light, though in the dark, there was no significant difference in the carbon and nitrogen status of the systems. The order of carbon saving was Chlorella > Tolyphthrix > Anabaena. Along with the saving of carbon, nitrogen fixation by these algae, the availablity of phosphate is greater in the inoculated sets than in the uninoculated ones. The increase in the available phosphate by the inoculation of algae may be due to that algae excrete some organic acids which might dissolve some of the phosphate. In addition, the organic phosphorus of the nucleic acid and nucleotide etc. of the algal material may be made available by the dephosphorylation. Thompson and Black[19] are of the opinion that dephosphorylation of these materials in soil might provide crops with appreciable amounts of phosphorus during the growing season.

In sets inoculated with Chlorella there is a slight greater increase in nitrogen than in control. It is interesting to note that though the Chlorella is not a fixer of nitrogen, even then it shows a small fixation of nitrogen in light. The probable reason of this seems to be that in soils Chlorella lives in symbiosis with nitrogen fixing organism Azotobacter[20] and during this process it supplies the Azotobacter with carbohydrate and the bacteria in turn, fixes nitrogen.

In the sets inoculated with Tolypothrix add Anabaena, there is appreciable increase in the nitrogen contents over that of control, and Chlorella sets, thereby having better efficiency, the increase being greater in the case of Tolypothrix than in that of Anabaena. This is in agreement with the general observation made by various algologists that Tolypothrix is a better fixer of nitrogen than Anabaena.

It is therefore concluded from our investigations that though algae can fix some atmospheric nitrogen in the soil, the amount is small and almost negligible in comparison to that fixed by organic materials undergoing slow oxidation in the presence of light.

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Influence of temperature on the hydrolysis of some naturally occurring rock phosphates and basic slags in conductivity water

By

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Abstract

It has been observed that Trichinopoly, Bihar and Algerian rock phosphates, and Tata, Kulti, German and Belgian basic slags are hydrolysed in conductivity water with the liberation of phosphoric acid and lime. The amount of phosphoric acid and lime passing into the solution increase with temperature. The results also show that more of lime than phosphoric acid passes into the solution with all these rock phosphates and basic slags. Therefore, these results establish that these naturally occurring rock phosphates and basic slags can serve both as liming agent and phosphatic fertilizer.

Introduction

The solubility of phosphatic fertilizers in water is probably the most widely operating factor influencing the ability to supply phosphorus to plants. In recent years a number of workers[1-8] have recommended the use of finely ground rock pho phates as fertilizer. The use of basic slag, a by–product of steel industry, as a fertilizer, started in 1884. The consumption of basic slag as a phosphatic fertilizer is second only to that of superphosphate.

Basic slag is a compound of tetra–calcium phosphate, silico–phosphate and silicates of lime and magnesia. According to Wagner[9] higher percentage of silica in basic slags increases the availability of P_2O_5 by 10–30%. Russell[10] remarked that silico–phosphate of basic slag will have different physiological action in the soil than ordinary mineral phosphates. According to Cameron & Bell[11] the efficiency of basic slags depends upon the degree of fineness to which it is ground. In addition to the P_2O_5 present, basic slag is valued for its content of lime, magnesia and some trace elements, which play an important role as soil conditioners and fertilizers.

According to Marshall, Reynolds, Jacob and Rader[12] the available P_2O_5 in calcined phosphate rock is 30% as against 20% in super phosphate. Hall and Morrison[13] observed that due to the presence of silica in basic slags, the phosphorus in slags is more effective than that in other phosphatic fertilizers. Scidenstucker[14] apprehended that whole of P_2O_5 present in basic slags may be soluble in water, but Walter[15] remarked that large quantities of water would be needed for the complete removal of P_2O_5 from basic slag. According to Sherman and Grant[16] the pH of the powdered slags varies directly with the number of excess moles of CaO present in the slag.

A survey of the available literature reveals that the influence of temperature on the hydrolysis of rock phosphates and basic slags has not been investigated. So, an attempt has been made by the authors to study the effect of temperature on

Trichinopoly, Bihar and Algerian rock phosphates, and Tata, Kulti, German and Belgian basic slags.

Experimental

1. Sample : Rock phosphates and basic slags employed in this investigation were analysed[17] and their composition is shown in table 1.

TABLE I

Rock Phosphates and Basic Slags	SiO_2 %	P_2O_5 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %
1. Trichinopoly rock phosphate	10·30	27·60	22·51	4·01	21·34	1·75
2. Bihar rock phosphate	5·65	27·96	21·18	3·87	11·95	0·78
3. Algerian rock phosphate	4·66	26·11	0·30	0·25	13·18	2·08
4. Tata basic slag	18·22	7·60	3·72	15·05	37·52	5·30
5. Kulti basic slag	23·00	4·49	3·05	14·33	45·67	6·15
6. German basic slag	16·04	17·85	2·38	14·05	43·60	5·02
7. Belgian basic slag	17·01	16·65	2·81	16·44	41·08	4·58

2. Solubility determination in water : 1·00 gm. of the rock phosphate or basic slag, sieved through a 200 mesh sieve, was taken in Jena glass bottles and 100 ml. of conductivity water were added to it. It was shaken in a mechanical shaker for one hour at the laboratory temperature. It was then placed in a thermostat maintained at 30°, 50° or 70°C for 5 hours after which the contents were filtered through a sintered funnel attached to a filtration flask and suction pump. For solubilities at temperatures 5° and 100°C, a Phillips refrigerator and water bath were used. Aliquot portions of the filtrate were utilised for the estimation of P_2O_5[18,19] and lime.[18] With another portion of the filtrate pH and electrical conductivity measurements were carried out.

A portable Cambridge pH meter and "Leitfahigkeitnsmesser" magic eye conductivity bridge (Laboratory model S. No. 177) were utilised for pH and conductivity determination respectively.

Result and Discussion

The results recorded in Tables 2a and 2b show that rock phosphates and basic slags when shaken with water are hydrolysed and liberate small amounts of phoshporic acid and lime into the solution. The results further show that the solutions of naturally occurring rock phosphates and basic slags are much richer in lime than phosphoric acid. German and Belgian basic slags have been found to contain more soluble phosphates than Indian basic slags which is due to the fact that foreign basic slags contain more of P_2O_5 than Tata or Kulti basic slags.

TABLE 2(a)

Temp. in °C	Trichinopoly Rock Phosphate				Bihar Rock Phosphate				Algerian Rock Phosphate			
	Millimoles/litre			Sp. Cond. in mhos X 10⁻⁴	Millimoles/litre			Sp. Cond. in mhos X 10⁻⁴	Millimoles/litre			Sp. Cond. in mhos X 10⁻⁴
	P_2O_5	CaO	pH		P_2O_5	CaO	pH		P_2O_5	CaO	pH	
5	0·0595	0·5913	7·80	1·35	0·0902	0·3095	7·55	1·68	0·1057	0·3544	7·30	1·61
30	0·0778	0·6621	7·85	1·77	0·0985	0·4132	7·65	1·96	0·1125	0·4340	7·40	2·15
50	0·1143	0·7893	8·00	2·73	0·1281	0·6527	7·80	2·63	0·1475	0·6179	7·50	2·92
70	0·1491	0·9017	8·10	3·70	0·1517	0·8675	7·95	3·48	0·1799	0·8318	7·60	3·85
100	0·1855	1·0526	8·20	4·39	0·1789	1·0502	8·15	4·09	0·2051	0·9936	7·80	4·71

TABLE 2(b)

Temp. in °C	Tata Basic Slag				Kulti Basic Slag				German Basic Slag				Belgian Basic Slag			
	Millimoles/litre			Sp. Cond. in mhos X 10⁻⁴	Millimoles/litre			Sp. Cond. in mhos X 10⁻⁴	Millimoles/litre			Sp. Cond. in mhos X 10⁻⁴	Millimoles/litre			Sp. Cond. in mhos X 10⁻⁴
	P_2O_5	CaO	pH		P_2O_5	CaO	pH		P_2O_5	CaO	pH		P_2O_5	CaO	pH	
5	0·0403	0·9019	8·05	1·95	0·0211	1·6324	8·60	2·75	0·0924	1·5921	8·55	3·08	0·0896	1·4217	8·50	2·97
30	0·0487	1·1664	8·35	2·21	0·0248	1·5900	8·85	3·49	0·1163	1·8253	8·65	4·47	0·1002	1·6344	8·55	3·84
50	0·0661	1·7033	8·65	3·33	0·0329	2·9714	9·10	4·36	0·1775	2·6910	8·75	7·27	0·1441	2·0323	8·70	5·11
70	0·0835	2·1183	8·85	4·18	0·0388	3·8971	9·35	5·48	0·2429	3·5187	8·90	9·18	0·1801	2·5525	8·80	6·46
100	0·1012	2·4900	9·10	5·25	0·0424	4·4566	9·65	6·73	0·3087	4·1266	9·00	11·95	0·2085	2·8607	8·90	7·52

All the rock phosphates have been observed to contain more soluble phosphate than Tata and Kulti basic slags. With Trichinopoly, Bihar and Algerian rock phosphates lesser amounts of lime pass into the solution than all the four basic slags.

The pH of the aqueous solutions of rock phosphates and basic slags are on the alkaline side and further shows an increase with temperature unlike the behaviour of calcium phosphate, whose pH decreases with temperature [20,21]. The increase in pH with temperature is a consequence of the solutions becoming richer in lime than P_2O_5. The electrical conductivity of the aqueous solutions of rock phosphates and basic slags show an increase with temperature. This may be due to the progressive liberation of Mg^{+2}, Ca^{+2}, HPO_4^{-2}, PO_4^{-3} and OH^- ions in solutions by the basic slags and rock phosphates.

When these rock phosphates or basic slags are added to the soil, the lime present in them readily decomposes phosphates of iron, aluminium, titanium, etc. as follows :

$$2\ FePO_4 + 3\ Ca(OH)_2 = Ca_3(PO_4)_2 + 2\ Fe(OH)_3$$
$$2\ AlPO_4 + 3\ Ca(OH)_2 = Ca_3(PO_4)_2 + 2\ Al(OH)_3$$
$$Ti_3(PO_4)_4 + 6\ Ca(OH)_2 = 2\ Ca_3(PO_4)_2 + 3\ Ti(OH)_4$$
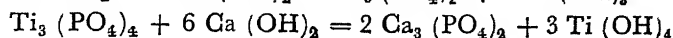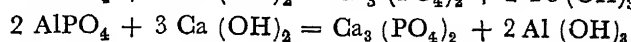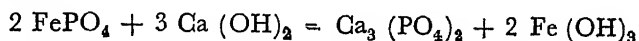
Thus, the basic slags and rock phosphates not only act as fertilizers by supplying small amounts of phosphoric acid on hydrolysis but also become producers of tri-calcium phosphate, which when freshly formed is a good source of available phosphates. Moreover, the low P_2O_5 solubility of rock phosphates and basic slags favours their availability over prolonged periods instead of restricting them to a single growing season, as is the case with soluble phosphates. For the same reason, in areas of heavy rain fall the basic slags and rock phosphates are less prone to leaching losses.

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Influence of Carbonic Acid on the Solubilization of some naturally occurring rock phosphates and basic slags

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Abstract

It has been observed that Trichinopoly, Bihar and Algerian rock phosphates, and Tata, Kulti, German and Belgian basic slags are decomposed to an appreciable extent by carbonic acid solutions. The increase in the solubility of these rock phosphates and basic slags is due to the fact that tricalcium phosphates present in them is converted into more soluble mono- and di- calcium phosphates and calcium bicarbonate. The rather abnormal increase in the solubility of basic slags has also been attributed to their silica content.

The amounts of soluble phosphoric acid and lime passing into the solution with rock phosphates have been observed to be smaller than Tata, German and Belgian basic slags in saturated solutions of carbonic acid. Therefore, it can be concluded from these results that basic slags are decidedly better fertilizers than naturally occurring rock phosphates.

Introduction

The various extraction methods to determine the availability of phosphate in soils have been based on the fact that plants can utilise different forms of soluble phosphates. The use of carbonated water has long been advocated for soil testing on the basis that plant roots produce CO_2 [1]. Machigin quoted by Brind[2] found that bubbling carbon dioxide for 2 hours through a 1:100 soil water suspension gave a better correlation with crop response to phosphorus than did the nitric acid method of Von Sigmond[3] or the 1% potassium carbonate method of Das[4].

Both carbonic and phosphoric acids have been found to play an important part as natural buffer mixtures in regulating the acidity of the soil as well as in the animal body. Moreover, in soil rich in organic matter, there is always appreciable production of carbonic acid which would react with the phosphate and thus give an indication of the availability of the phosphates.

In view of the above an attempt has been made by the authors to study the solubilisation of Trichinopoly, Bihar and Algerian rock phosphates and Tata, Kulti, German and Belgian basic slags, in carbonic acid solutions.

Experimental

1. *Sample* : The Composition of all the naturally occurring rock phosphates and basic slags utilised in these experiments is the same as described by the authors in their communication[5] dealing with the influence of temperature on the hydrolysis of these materials.

[361]

TABLE 1(a)

Temperature 30 ± 0·1°C

Conc. of Carbonic acid in normality	Trichinopoly rock phosphate				Bihar rock phosphate				Algerian rock phosphate			
	Millimoles/litre			Sp. Cond. in mhos. X 10-4	Millimoles/litre			Sp. Cond. in mhos X 10-4	Millimoles/litre			Sp. Cond. in mhos. X 10-4
	P_2O_5	CaO	pH		P_2O_5	CaO	pH		P_2O_5	CaO	pH	
0·0013	0·1188	1·1780	7·70	2·29	0·1376	0·7135	7·50	2·31	0·1613	0·6798	7·25	2·70
0·0024	0·1536	1·6008	7·60	2·69	0·1684	0·9725	7·40	2·59	0·2024	0·8842	7·15	3·06
0·0038	0·1821	1·9855	7·55	3·06	0·1930	1·1839	7·35	2·82	0·2377	1·0293	7·10	3·38
0·0050	0·2073	2·2500	7·50	3·47	0·2122	1·3074	7·30	3·02	0·2680	1·1286	7·05	3·68
0·0078	0·2321	2·4342	7·45	3·89	0·2243	1·3825	7·25	3·45	0·2848	1·1903	6·95	4·17

TABLE 1(b)

Temperature 30 ± 0·1°C

Conc. of Carbonic acid in normality	Tata basic slag				Kulti basic slag				German basic slag				Belgian basic slag			
	Millimols/litre			Sp. Cond. in mhos. X-4	Millimols/litre			Sp. Cond. in mhos X-4	Millimols/litre			Sp. Cond. in mhos X-4	Millimols/litre			Sp. Cond. in mhos X-4
	P_2O_5	CaO	pH		P_2O_5	CaO	pH		P_2O_5	CaO	pH		P_2O_5	CaO	pH	
0·0013	0·1776	3·0521	8·00	5·08	0·0542	4·3747	8·60	5·99	0·3043	3·7511	8·40	8·35	0·2681	3·5447	8·35	7·06
0·0024	0·2675	4·6911	7·75	7·36	0·0787	6·1415	8·50	8·13	0·4391	5·4739	8·25	11·34	0·3902	5·3002	8·20	9·36
0·0038	0·3562	6·0616	7·60	9·25	0·1016	7·6774	8·40	10·11	0·5517	7·0150	8·10	14·06	0·4995	6·6130	8·10	11·33
0·0050	0·4335	7·2505	7·50	10·51	0·1236	9·0713	8·35	12·01	0·6673	7·9413	8·00	16·18	0·5714	7·5095	8·05	13·17
0·0078	0·4862	8·0571	7·35	12·35	0·1390	9·9430	8·25	14·41	0·7551	8·6378	7·85	18·95	0·6306	8·0092	7·95	15·86

2. *Solubility determinations* :   1·00 gm of the rock phosphate or basic slag was shaken with 100 ml of carbonic acid solution in a 250 ml. Erlenmeyer flask for one hour in a mechanical shaker and then allowed to stand in a thermostat maintained at 30°C for five hours. After this the solution was filtered and aliquot portions were utilized for the estimation of P_2O_5 [6,7] and lime[6] and the determination of pH and electric conductivity.

The pH of the solutions were determined by Portable Cambridge, pH meter and the electric conductivity by "Leitfahigkeitsmesser" magic eye conductivity bridge.

Carbonic acid solutions were prepared by bubbing carbon dioxide in double distilled water for 1 hour, 2 hours, 3 hours, 5 hours and 24 hours and their strengths were determined by titrating against standard baryta solution[8].

Result and Discussion

The solubility of rock phosphates and basic slags has been found to increase by the action of carbonic acid solutions. Results show that even small concentrations of carbonic acid are able to decompose the phosphate present in basic slag to an appreciable extent. The amounts of P_2O_5 passing into the solution with Tata, Kulti, German and Belgian basic slags in water at 30°C are 0·0487, 0·0287, 0·1163 and 0·1002 millimoles per litre respectively[5]. This shows that the P_2O_5 solubility approximately increases 10, $5\frac{1}{2}$, $6\frac{1}{2}$ and 6 times in saturated solutions of carbonic acid for Tata, Kulti, German and Belgian basic slags respectively. The CaO concentrations also markedly increase with all these basic slags. The amounts of CaO passing into the solution at 30°C with Tata, Kulti, German and Belgian basic slags in water are 1·1664, 1·9900, 1·8253 and 1·6344 millimoles per litre respectively[5]. It is evident from these values that the percentage increase of P_2O_5 is greater than that of CaO.

There has been a slight increase in the solubility of Trichinopoly, Bihar and Algerian rock phosphates in carbonic acid solutions. The amounts of P_2O_5 and CaO gradually increase in different concentrations of carbonic acid. The results show that the solubility of rock phosphates is much less pronounced than that of basic slags. The amounts of P_2O_5 and CaO passing into the solution in saturated solution of carbonic acid with all these rock phosphates are smaller than with Tata, German and Belgian basic slags. Thus from Carbonic acid solubility point of view basic slags appear to contain more available P_2O_5 than rock phosphates. These results, therefore, establish that if carbonic acid is used as a yardstick, basic slags are decidedly better fertilizers than naturally occurring phosphate rocks because they can serve both as a phosphate fertilizer and as a liming agent in soils which are deficient in lime or suffer from the excess of acidic salts.

Lyon and Buckman[9] have attributed the dissolving action of carbonic acid on rock phosphates and basic slags to the following equations :

Rock phosphate
$$[Ca_3(PO_4)_2] 3 CaCO_3 + 6H_2CO_3 = 3 Ca(H_2PO_4)_2 + 7 CaCO_3.$$

Basic Slag
$$(CaO)_5. P_2O_5. SiO_2 + 8 CO_2 + 6 H_2O = Ca(H_2PO_4)_2 + 4 Ca(HCO_3)_2 + SiO_2.$$
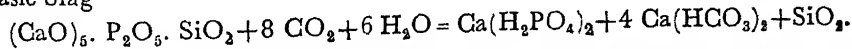
It appears from our experimental results that as these materials contain free lime and calcium carbonate in considerable quantities, a part of the carbonic acid converts them to more soluble calcium bicarbonate, which accounts for the excess of lime in the solution. Moreover, the conversion of tricalcium phosphate present

[363]

in these materials to calcium bicarbonate by another part of the carbonic acid is possible because the first dissociation constant of phosphoric acid ($K_1 = 1.0 \times 10^{-2}$, $K_2 = 7.5 \times 10^{-8}$ and $K_3 = 4.8 \times 10^{-13}$) is considerably higher than the total dissociation constant of carbonic acid ($K_1 = 3.5 \times 10^{-7}$ and $K_2 = 4.4 \times 10^{-11}$). The conversion of this tricalcium phosphate to more soluble mono– and di–calcium phosphates is responsible for the increase in the P_2O_5 solubility of these materials. But this alone does not seem to explain the rather abnormal increase in the solubility of basic slags. Therefore, we are of the opinion that this is due to the complex composition of the basic slags. It is likely that silica in the form in which it present in basic slags plays a major role in rendering the lime and phosphate of slags soluble in presence of carbonic acid.

Acknowledgments

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Effects of glucose and peat on the solubilisation of some naturally occurring rock phosphates and basic slags

By

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Abstract

The solubility of Trichinopoly, Bihar and Algerian rock phosphates, and Tata, Kulti, German and Belgian basic slags has been found to increase markedly in presence of decomposing glucose and peat with lapse of time. This is due to the fact that various organic acids and carbonic acid which are produced during the decomposition of these organic matter play an important part in the conversion of less soluble tricalcium phosphate present in these materials to more soluble mono- and di- calcium phosphates. These results are also supported by the electric conductivity measurements. The increase in the solubility is much more in the glucose system than in the peat system. It has been observed that there is a definite correlation between the pH of the system and the amount of P_2O_5 released in solution.

Introduction

From times immemorial organic matter has been profitably applied in crop production. In the recent paper Stelmach[1] has discussed the effect of organic matter on soil fertility. Moreover, Wu and Ma[2] have reported that organic manures in soil increase external surface area, decrease electrophoretic velocity, decrease phosphorus fixation, increase content of easily released ammonia and increase available water holding capacity. Collings[3] has rightly emphasised the importance of organic matter as "Nearly all soils are benefitted by the additions of suitable organic matter, no matter how much they contain. It is a well known fact that soils high in organic matter contain more phosphorus readily available to plants than do soils low in organic matter."

Dhar *et al*[4] have established that organic substances like molasses, sugars, straw, peat, finely divided bituminous coal etc. not only improve physical structure of the soils but undergo slow oxidation to liberate energy which is utilised in fixing atmospheric nitrogen and enriching the nitrogen status of soil. They have further observed that in the presence of large amounts of calcium phosphate, finely divided basic slags or rock phosphates more or less stable phospho-proteins are formed by the combination of protein and phosphorus compounds and they resist the loss of nitrogen. Moreover, all the plant nutrients *i.e.* nitrogen, potash, phosphate, lime and trace elements are supplied to crops by this mixture and the fertility of the soils is greatly enhanced.

The advantages of adding organic matter along with phosphatic fertilizers are widely realised. This information has been derived from the plant uptake and response data. Dhar[5], Levin[6], Sandhoff[7] and others[8-12] have reported that by the addition of phosphate and organic matter to the soil much better results are obtained than either of them when used alone. Observations made by Copeland and Merkle[13], Midgley and Dunklee[14] and others[15,16] have indicated that organic

matter increases the availability of soil phosphates and rock phosphates when added to soil as a fertilizer.

In view of the above literature, authors made an attempt to study the solubilisation of Trichinopoly, Bihar and Algerian rock phosphates, and Tata, Kulti, German and Belgian basic slags in presence of decomposing organic matter like glucose and peat.

Experimental

1. *Sample* : The composition of rock phosphates and basic slags utilised in this investigation is the same as described by the authors[17] in their paper dealing with the influence of temperature on the hydrolysis of these materials.

2. *Solubility determinations* : 1·00 gm of the rock phosphates or basic slags, sieved through a 200 mesh sieve, was taken in 250 ml Erlenmeyer flasks. To these 0·4 gm carbon was added as glucose or peat. 20 ml of distilled water were added and the moisture content was maintained throughout the experiment. The flasks were kept under 500 watt bulb hung at a distance of two feet from the flasks. Different sets of flasks were used for different intervals of time. The contents of the flasks was stirred daily. After definite intervals of time, the total water content of the flasks was made upto 100 ml. The flasks were then shaken for one hour in a mechanical shaker and then allowed to stand for some time. The contents were then filtered. Aliquot portions of the filtrate were utilised for determining P_2O_5[18,19] lime [18], pH and electric conductivity.

For the estimation of P_2O_5 and lime aliquot portion of the filtrate was taken in a 250 ml beaker and to this were added 5 ml of conc. HNO_3 to oxidise the organic matter. The solution was evaporated to dryness. The process was repeated till the whole organic matter was oxidised. The residue was then moistened with 5 ml of conc. HNO_3 and warmed to dissolve the residue. The solution was then diluted and then used for estimating P_2O_5 and lime.

The glucose and peat utilised in these experiments contained 39·94 and 34·56% total carbon respectively.

Result and Discussion

From the data recorded in the Table 1a and 1b the effect of decomposing organic matter *viz.* glucose and peat on the solubility of naturally occurring rock phosphates and basic slags becomes evident. The results show that the increase in the solubility of all these materials is much more in glucose system than in peat system, which is due to the fact that glucose being soluble carbohydrate is readily oxidised whereas peat is not easily oxidised.

The pH of the solutions has been found to decrease with lapse of time. The results show that there is more fall in the pH values with the glucose system than with the peat system. Similar trend occurs in the release of P_2O_5 by these systems. This clearly indicates that there is a difinite correlation between the pH of the system and the amount of P_2O_5 into the solution. Lower the pH of the system more is the amount of P_2O_5 in the dissolved state.

The electrical conductivity measurements show that there is an increase in the values with the passage of time. The increase in the electrical conductivity of the resulting solutions of basic slags and rock phosphates with the decomposition of glucose and peat is due to the fact that more ions are passing into the solution with lapse of time. These ions are furnished by the dissolving rock phosphates and basic slags as well as the decomposition products of these organic substances *i.e.* organic acids produced as intermediate products[20,21] and final product carbonic acid.

TABLE 1(a)

Glucose System

Number of days	Trichinopoly rock phosphate Millimoles/litre				Bihar rock phosphate Millimoles/litre				Algerian rock phosphate Millimoles/litre			
	P_2O_5	CaO	pH	Sp. Cond. in mhos ×10⁻⁴	P_2O_5	CaO	pH	Sp. Cond. in mhos ×10⁻⁴	P_2O_5	CaO	pH	Sp. Cond. in mhos ×10⁻⁴
50	0·1675	1·9356	6·50	3·02	0·1806	1·0791	6·35	2·46	0·2268	0·9341	6·10	3·95
150	0·2654	3·8007	5·95	6·36	0·3308	2·6890	5·80	4·92	0·3957	2·3072	5·70	7·30
250	0·2985	4·5472	5·60	7·11	0·3802	3·1991	5·55	5·53	0·4416	2·9002	5·50	8·10
Peat System												
100	0·1483	1·3255	7·25	3·44	0·1615	0·8820	7·05	4·22	0·1951	0·9706	6·90	4·68
200	0·2013	1·5425	7·00	4·16	0·2226	1·0834	6·80	4·90	0·2678	1·2093	6·65	5·40
300	0·2300	1·7930	6·85	4·60	0·2625	1·2209	6·65	5·62	0·3128	1·4670	6·50	6·09

TABLE 1(b)

Glucose System

Number of days	Tata basic slag Millimoles/litre				Kulti basic slag Millimoles/litre				German basic slag Millimoles/litre				Belgian basic slag Millimoles/litre			
	P_2O_5	CaO	pH	Sp. Cond. in mhos ×10⁻⁴	P_2O_5	CaO	pH	Sp. Cond. in mhos ×10⁻⁴	P_2O_5	CaO	pH	Sp. Cond in mhos ×10⁻⁴	P_2O_5	CaO	pH	Sp. Cond. in mhos ×10⁻⁴
50	0·4014	6·9527	6·75	11·15	0·1126	8·6891	7·25	13·27	0·6194	7·6058	6·90	15·93	0·5585	7·3625	7·00	14·72
150	0·6453	10·6374	6·00	16·28	0·1916	13·7662	6·70	20·05	0·9972	12·4945	6·30	23·02	0·8519	12·0552	6·45	20·98
250	0·7518	12·0714	5·75	18·90	0·2312	15·2412	6·65	23·02	1·1128	13·9154	6·15	25·63	0·9430	13·4792	6·30	23·70
Peat System																
100	0·1593	3·0384	7·65	5·31	0·0628	4·5519	8·10	7·45	0·2554	3·7742	7·90	8·20	0·2236	3·5002	7·85	7·80
200	0·2465	4·2378	7·40	6·35	0·0802	5·9590	7·95	8·57	0·3954	5·0448	7·70	9·38	0·3442	4·6765	7·65	8·72
300	0·3281	5·0375	7·25	7·18	0·1092	6·8472	7·80	9·50	0·4989	5·9821	7·55	10·32	0·4334	5·4503	7·51	9·65

It has been observed that the amounts of P_2O_5 passing into the solution with Tata, German and Belgian basic slags are always greater than with Trichinopoly, Bihar and Algerian rock phosphates. Thus in the presence of decomposing organic matter basic slags appear to contain more available P_2O_5 than naturally occurring rock phosphates. Also, greater amounts of lime, have been observed to pass into the solution with basic slags than with rock phosphates. These results, therefore, point out the great utility of basic slags, both as a phosphatic fertilizer and as a liming agent.

It is interesting to note that in crop production all over the world basic slags have been found to be more efficient than rock phosphates. Results obtained at Kentucky Experimental Station indicate that basic slag is 85 to 100% as effective as superphosphate.

Dhar and coworkers[22] have recently advanced the view that the application of organic matter along with phosphates improves the soil fertility. They have further observed that the available phosphate status of soils increases markedly when decomposing organic matter is supplemented with basic slags or naturally occurring rock phosphates. This observation is in agreement with our experimental findings. Similarly Selezn'ov[23] reported that the addition of peat increased phosphorus availability in soils. Hsu and Yeu[24] observed that in green house experiments application of peat in some cases increased yields and soil physical properties were also improved.

The increase in the solubility of rock phosphates and basic slags is due to the fact that tri-calcium phosphate present in them reacts with carbonic acid, formed during the decomposition of organic matter, according to the following equations :

$$Ca_3(PO_4)_2 + 2H_2CO_3 = 2CaHPO_4 + Ca(HCO_3)_2$$
$$2CaHPO_3 + 2H_2CO_3 = Ca(H_2PO_4)_2 + Ca(HCO_3)_2$$
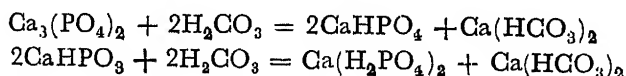
Similar reactions may take place with organic acids which are also produced during the oxidation of glucose and peat. Thus the less available phosphates of calcium present in these materials are made available to plants due to the formation of mono and di- calcium phosphates in presence of decomposing organic matter.

Thus it can be concluded from our experimental results that the future of permanent agriculture all over the world depends upon a proper utilisation of all types of organic substances mixed with naturally occurring rock phosphates or basic slags.

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Studies in Alkali Soil Profile

By

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Abstract

The alkali soil profile collected from Phulpur, (Allahabad) is characterised by marked horizon differentiation, accumulation of exchangeable bases in the lower horizons, dominance of soluble Na over Ca and Mg cations and of carbonate and bicarbonate over chloride and sulphate anions and increase of clay content from top to lower horizons.

The result of soil forming forces working for long periods of time is the gradual differentiation of layers or horizons within the parent material. Collectively these horizons are called a "Profile". Since the soil profile represents the result of all the soil forming processes, it is the natural unit of study. Raychaudhari and Coworkers[1] have shown that the saline soils of Delhi state are characterised by the absence of horizon differentiation and structural formation. The main anions present in the saturation extracts of these soils were chloride and sulphate. Mehta[2] observed that in the long area of the Punjab, there was invariably a salt bearing layer, some distance below the surface, the main salt being sodium sulphate.

The nature of saline and alkaline soils of Indian Indo-Gangetic alluvium has been studied by Mukherji, Agarwal and Mukherji[3], Mukherji and Agarwal[4], Agarwal and Mehrotra[5] and by Agarwal and Yadava[6]. Recently Dhar and Singh[7] studied the saline and alkaline soils of Rajasthan state and found that these soils possess characteristic properties of the degraded chernozem soil types of Russia.

With a view to elucidate the process of the formation of the alkali soil in this area of Allahabad district, the present investigations were undertaken.

Experimental

The profile for the present investigation was brought from a village situated at a distance of 18 miles from Allahabad. The horizons were first determined by colour differences and these were further subdivided according to the structure, texture and concentrations and samples were taken from each of these subhorizons. Soil sampling was carried on by digging the two sides upto a depth of 6" and taking out 12" < 6" × 6" pillar like soil columns, avoiding any mixing of the representative samples. Ironoxide and sesquioxide were estimated by the methods described by Wright[8]. Calcium, magnesium, potassium and phosphorus were estimated by the methods described by Piper[9]. Carbon and nitrogen were estimated by Robinson, McLean and Williams method[10] and salycylic acid reduction method[11] respectively. $CaCO_3$ equivalent and soluble salts were determined by Richards method[12]. Hissink's method[13] was used for the determination of exchangeable calcium and magnesium. Exchangeable sodium was determined in

mmonium acetate extract by Kahane's method[14] and potassium in sodium chloride extract by the method described by Piper[9]. Electrical conductivity was determined by a Leeds and Northrup Pt–Ir drum type bridge method[15] and pH was determined by Beckman pH meter[16]. Pipette method[17] was followed for mechanical analysis of soil. Dispersion factor was determined by Puri's method[18]. Permeability and water holding capacity were determined by the method quoted by Piper[9].

Results

Description of the Profile

Date of collection	20th March, 1962
State	Uttar Pradesh.
Country	India.
Soil type	Alkali.
Geographical land-scape.	About two and a half miles from Babugarj Bus station (Phulpur), Allahabad.
Geology	Alluvial origin.
Microrelief	Plain field where nothing was grown due to alkalinity and which we selected for our field experiments.
Condition and culture.	Whitish patches all over the area. Few patches of grass like Cyanoden dactylon were observed. Unfit for cultivation due to alkalinity.

TABLE I

Morphological features of the Alkali soil profile

Horizon	Depth in inches	Description
A	0–6	Whitish grey, sandy loam, friable, dry, few grass roots present, alkaline in reaction.
B	6–18	Brownish gray with whitish, patches, sandy loam, hard, porous, dry, alkaline in reaction.
B_1	18 30	Dark grey, clayey loam, structurel ss, compact, dry, small size calcoreous nodules pres nt, alkaline in reaction.
B_2	30–42	Brownish grey, clayey loam, structureless, compact, dry, big size calcareous nodules present, alkaline in reaction.
B_3	42–54	Yellowish clayey loam, structureless, compact, dry, big size calcareous nodules present, alkaline in reaction.
Co	54–66	Yellowish brown, sandy loam, soft, sticky, dry, big size calcareous nodules present, alkaline in reaction.
C_1	66–78	Light yellow, sandy loam, soft, sticky, wet, big size calcareous nodules present, alkaline in reaction.

TABLE 2
Percent chemical composition of the alkali soil profile

| | DEPTH IN INCHES | | | | | | |
	0–6	6–18	18–30	30–42	42–54	54–66	66–78
Loss on ignition	2·65	2·82	3·04	4·80	5·10	5·30	3·62
HCi insoluble	84·32	83·40	81·25	41·95	68·05	75·86	79·00
Sesquioxide	7·15	8·12	10·34	13·25	11·30	11·82	10·65
Fe_2O_3	4·12	4·45	4·62	6·50	4·90	5·32	5·82
CaO	1·26	1·24	1·28	5·45	11·20	5·25	4·96
MgO	1·23	1·33	1·45	1·65	1·80	0·60	0·58
K_2O	0·79	1·15	1·30	1·52	1·86	0·80	0·72
P_2O_5	0·135	0·145	0·168	0·170	0·186	0·138	0·126
$CaCO_3$ equivalent	2·48	1·75	2·20	10·50	17·00	10·35	4·42
Carbon	0·2108	0·1946	0·1805	0·1802	0·1778	0·1776	0·1568
Nitrogen	0·040	0·040	0·034	0·030	0·030	0·026	0·026

TABLE 3
Composition of the saturation extract of the alkali soil profile

(Soluble cations and anions of the saturation extract m.e./litre)

| | DEPTH IN INCHES | | | | | | |
	0–6	6–18	18–30	30–42	42–54	54–66	66–78
Saturation %	54·00	56·20	58·00	60·52	57·50	52·00	48·20
Ca^{++}	144·50	148·60	150·20	185·40	160·00	125·20	85·40
Mg^{++}	70·60	71·40	72·20	74·80	73·50	71·00	62·70
Na^+	1650·20	1662·50	1250·50	1160·20	954·40	856·50	640·20
K^+	0·85	1·20	0·96	0·90	0·72	0·56	0·50
Total cations	1866·15	1883·70	1473·86	1421·30	1188·60	1053·36	788·50
CO_3	546·50	538·60	440·60	425·60	340·40	298·50	215·50
HCO_3^-	580·00	596·40	492·80	476·40	365·60	325·40	226·40
Cl^-	418·50	420·40	315·40	308·60	286·60	262·40	198·00
SO_4^{--}	320·20	323·60	218·60	210·20	185·40	152·00	132·50
Total anions	1865·20	1979·00	1467·40	1420·80	1178·00	1038·30	772·40

TABLE 4
Exchangeable bases in alkali soil profile

	0–6	6–18	18–30	30–42	42–54	54–66	66–78
Base exchange capacity m.e. %	14·54	15·65	17·30	19·65	15·52	12·23	11·45
Exch. Ca, m.e. %	4·62	5·23	6·65	8·05	7·15	5·25	4·85
Exch. Mg., m.e. %	1·70	1·55	1·95	2·75	2·62	2·46	2·40
Exch. K, m.e. %	0·20	0·26	0·28	0·32	0·36	0·30	0·34
Exch. Na. m.e. %	7·52	7·85	8·05	8·42	4·26	2·65	2·42
Ca–saturation ratio %	31·70	33·20	38·40	40·90	46·00	42·90	42·30
Na–saturation ratio %	51·80	50·10	46·50	42·80	27·40	21·60	21·10
Exch. Na / Exch. Ca. %	162·70	150·00	121·00	104·50	59·50	50·40	49·80

TABLE 5

	0–6	6–18	18–30	30–42	42–54	54–66	66–78
Electrical conductivity in 25°C	11·85	12·20	11·75	11·02	10·32	9·20	8·15
M.mhos/cm at pH	9·30	9·50	9·40	9·20	9·10	9·00	8·80
Soluble sodium %	88·40	88·20	84·80	81·60	80·20	81·30	81·10
Sodium adsorption ratio	159·28	158·63	118·64	101·77	88·37	86·51	74·59
Exch. sodium ratio	0·93	0·99	1·14	1·33	2·64	3·61	3·73

TABLE 6
Mechanical analysis, water holding capacity, dispersion factor and permeability of alkali soil profile

	0–6	6–18	18–30	30–42	42–54	54–66	66–78
Coarse sand % (2·0 – 0·2 mm.)	8·45	2·62	2·40	1·65	1·70	9·46	17·54
Fine sand % (0·2 – 0·2 mm.)	43·50	40·00	25·24	21·45	22·45	38·54	48·62
Silt % (0·02 – 0·002 mm.)	32·50	40·20	47·52	49·82	48·32	26·62	20·42
Clay % (Less than 0·002 mm.)	13·10	15·10	21·62	24·45	23·42	23·35	8·82
Water holding capacity %	46·25	48·54	58·65	54·42	51·25	43·43	37·54
Disperson factor %	15·35	16·70	19·52	20·20	17·62	15·40	13·62
Permeability c.c. per hour	4·20	3·80	3·00	2·80	3·40	5·50	7·60

Discussion

The chemical composition results have been recorded in table 2. There is a significant increase in the sesquioxide and iron oxide contents from top to fourth horizon (30–42″). The lime and magnesia contents are very low in the top horizons but increase in the lower horizons indicating leaching down of these bases from the top horizon and their accumulation in the lower ones. Calcium carbonate percentage increases with depth and is highest in the fifth horizon (42–54″). Calcium under the influence of leaching mobilizes into the lower horizons of the alkali soil profile and is precipitated there as $CaCO_3$ due to alkalinity which is evident as *Kankar* in the morphological features of the profile (table 1). The soil is poor in organic carbon and total nitrogen contents. The percentage of phosphate and potash is very low.

Analysis of the saturation extract of this profile (table 3) shows that amongst the cations, soluble sodium dominates the divalent cations Ca and Mg and that amongst the anions, carbonate and bicarbonate dominate chloride and sulphate. This makes the soil alkaline.

Results obtained for exchangeable bases are recorded in table 4. The base exchange capacity of the layers (6–18″), (18–30″), (30–42″) and (42–54″) is greater than in the other horizons. This may be due to the accumulation of clay colloids in the above mentioned horizons. The amount of exchangeable sodium is high exceeding the amount of exchangeable divalent bases Ca and Mg. Concentration of exchangeable Ca and Mg is highest in the lower horizons, which may be due to the fact that the cations might have leached down in the lower layers. Ca–saturation ratio varies from 31·7 to 46·0% and Na-saturation ratio varies from 51·8 to 21·1%. The ratio of adsorbed sodium to calcium varies from 49·8 to 162·7 Taylor and Mehta[19] reported that deterioration of the soils of the Punjab is chiefly due to the formation of a zone of accumulation of soluble salts.

Table 5 shows that electrical conductivity and pH decrease from top to the bottom after the second horizon (6–18″). The values of sodium adsorption ratio (S.A.R.), recorded in table 5, range between 74·52 to 159·28 and due to the increase in the amounts of soluble Ca and Mg, the sodium adsorption ratio decreases with depth. The sodium adsorption ratio is defined as

$$\frac{Na^+}{\sqrt{\dfrac{Ca^{++} + Mg^{++}}{2}}},$$

where the designated cations refer to the concentration of the individual soluble cations in the saturation extract expressed in m.e./litre and the exchangeable sodium is defined as the ratio between the cation exchange capacity minus exchangeable sodium.

Results obtained for the mechanical composition and some physical properties are recorded in table 6. The percentages of coarse and fine sand decrease upto the fourth horizon (30–42″, and then increases, the maximum being present in the two lowermost horizons. Clay and silt percentage increases from top to bottom upto the fourth horizons (30–42″) Clay seems to have been elluviated into the fourth horizon which has been graphically shown in Fig. 1. This generally takes place due to the mobile dispersive action of clay. Water holding capacity was observed maximum in the third horizon (18–30″). The dispersion factor increases and permeability decreases with the increase of clay content which has been graphically presented in Fig. 2. In the fourth horizon (30–42″), clay percentage and dispersion factor are maximum whereas permeability is minimum.

Fig. 2

DISPERSION FACTOR AND PERMEABILITY

OF ALKALI SOIL PROFILE

PERMEABILITY cc/hr. SCALE ICC=2mm   DISPERSION FACTOR SCALE
1%=2mm

DEPTH IN INCHES : SCALE 1 INCH = 1 mm.

Fig. 1

DISTRIBUTION OF SILT AND CLAY IN

AIKALI SOIL PROFILE

SILT PERCENT : SCALE 1%= 1m.m.

CLAY PERCENT : SCALE 1%= 1 m.m.

DEPTH IN INCHES : SCALE 1INCH = 1 m.m.
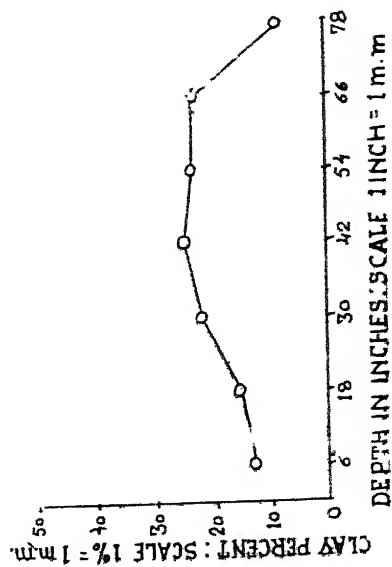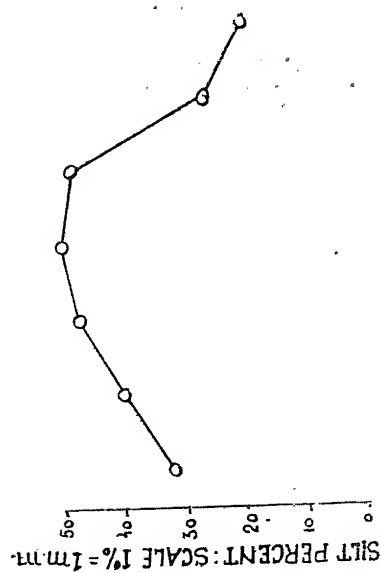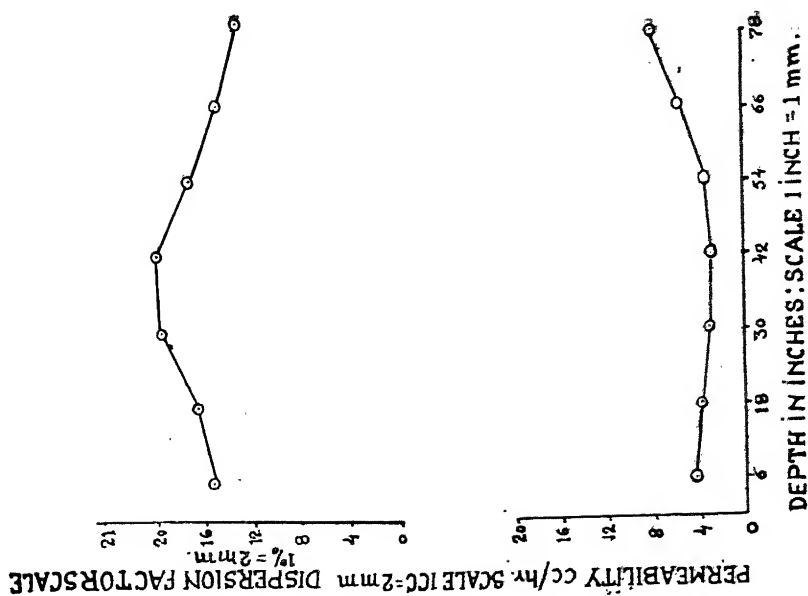
Chang and Dregne[20] noted an increase in dispersion ratio and moisture retention of soil with increasing levels of exchangeable sodium percentage. Longenecker and Lyerly[21] observed that reductions in soil permeability were directly proportional to the amount of swelling, which was the result of the degree of sodium saturation on the exchange complex.

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Role of Light energy, organic matter and Rock Phosphate in the fixation of atmospheric Nitrogen in Alkali soil

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Abstract

The role of light energy, organic matter and rock phosphate in fixation of atmospheric nitrogen in alkali soils from Soroan (Allahabad) has been studied. The sources of organic matter were spent wash (Molasses), saw dust, wheat straw and Swedish Peat and that of rock phosphate from India. The efficiency of nitrogen fixation *i.e.* the amount of nitrogen fixed in mg. per gram of Carbon Oxidised was always found greater in the presence of light than in the absence of it. Addition of rock phosphate increases the efficiency of nitrogen fixation as well as rate of carbon oxidation both in the presence as well as in the absence of light energy. Organic materials like saw dust, wheat straw and Swedish Peat are useful in maintaining the humus status of the highly alkaline soil and side by side the status of available phosphorus and exchangeable calcium was raised considerably. The pH of the soil decreased from 10·6 to 8·0 and was an appreciable change in the reclamation of alkali soils.

Likewise atomic energy, light energy is distributed in quanta. When light energy is absorbed in a quanta by a molecule, an electron may be displaced to an outer orbit of the electronic configuration of an atom or a molecule thus the potential energy rises. When the energy absorbed is sufficient it may displace the electron altogether and the energy absorbed may be remitted and may cause to induce a chemical change or possibly the energy absorbed by a molecule may be transferred to adjacent molecule as it happens in the process of photosynthesis *i.e.* the transfer of energy from xanthophyll to chlorophyll. Van Niel (1941) reported the splitting of water molecule by light energy absorption in the process of photosynthesis in plant.

$$4 \ H_2O + \text{Light energy} = 4 \ (H) + 4 \ (OH)$$
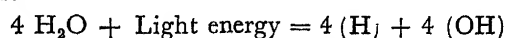
Similar observations have been reported by Franck (1955) and Vishniac and Rose (1958) using water labelled with the radio active hydrogen isotope, tritium. In the presence of light the chlorophyll became radio active while in the dark it did not become radio active. Formaldehyde, CH_2O was the obvious intermediate product in the process of photosynthesis *i.e.* the photolysis of water molecule and the fixation of carbon as carbon dioxide for not only is it in the simplest substance containing carbon, hydrogen and oxygen in the same proportion in which they are found in carbohydrate, but is also known to condense under certain conditions to form sugars. Later on Calvin and his collaborators put forth the hypothesis of formation of the intermediate products phosphoglyceric acid and ribose

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diphosphate. Light energy has proved a very effective tool in the synthesis of food material in the plant kingdom specially the carbohydrates and fats. How the proteins and aminoacids are formed is a question to be given a consideration. Although the plants are surrounded by unlimited supply of elemental nitrogen, but are unable to utilise it directly unlike carbon and oxygen.

The world literature on soil microbiology reports that the bacteria are able to fix nitrogen in the soil *viz.* symbiotically the Rhizobium species and non-symbiotically the Azotobacter and clostridium species ; that is to say that they are able to assimilate the free nitrogen of the air. But no literature reports the nature of the mechanism as to how the process takes place. No literature has succeeded in demonstrating that the bacteria is able to fix nitrogen, when grown by itself ; on the other hand the literature says that the bacteria can grow well when supplied with combined nitrogen in the form of ammonium sulphate or nitrate. Therefore this can safely be said here that the bacteria does not fix the atmospheric nitrogen but it eats away the combined nitrogen fixed from the other sources in the soil. No life is possible to exist without oxygen and nitrogen was not reported to be used in elemental form by any or living organism, Lavoisier (1781). The chief categories of soil organisms reported to occur in the soil are Bacteria, Actinomycetes, Fungi and Protozoa. They have been reported to feed on soil humus and upon combined form of nitrogen ammonia and nitrate and sometimes they are parasite of one another for their existence. Algae are widely distributed in the soil but they are chlorophyll bearing and manufacture their own food.

The reduction of nitrate in the green leaf of a plant has been described due to photochemical reaction as the process was found to be accelerated in the presence of light with the help of certain enzymes and adenosine triphosphate by plant physiologists. The reduced ammonia forms amines and amino acids and protein is synthesised in the plant body :

$$COOH \ (CH_2)_2 \ CHNH_2 \ COOH \ +NH_2 \longrightarrow$$
Glutamic acid

$$CONH_2 \ (CH_2)_2 \ CHNH_2 \ COOH$$
Glutamine
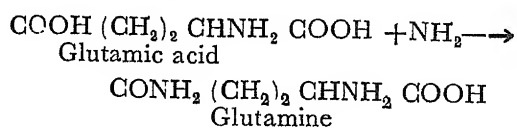
A process known as transamination from glutamic acid several other aminoacids are formed by transfer of aminogroup attached to different carbon atoms. The synthesis of proteins in the plant may be aided by photochemical reaction since the light plays its role in the reduction of nitrate into nitrite and finally into ammonia is well known to plant physiologists. The above review tells that the plant manufactures major parts of the food material by fixing atmospheric carbon using light energy of the solar system. Nitrogen as one of the chief consitituent of protein in the plant comes from the soil, this is now certain. The problem of nitrogen supply and its availability in the soil is a world wide problem. The nitrogen added as fertiliser a major part of it is lost due to leaching, volatilisation and adsorption in the clay complexes and also humus. Puhr (1945) reported that addition of sodium nitrate did not maintain the level of nitrogen nor increased the crop yield in South Dakota experiment Station U. S. A. The world literature on soil fertility of nitrogen element show that the soils rich in humus are rich in nitrogen. The soil under forest cover, grass lands and prairies contain much accumulated humus with higher nitrogen content than soil under cultivation. White *et al* (1945) reported the level of nitrogen in Pennsylvania grass land soils 68% greater than soil under cultivation. Shutt (1925) in Canada has shown the loss of nitrogen ranging up to 75 pounds per acre annually in addition to that removed

by crops in the soils Manitoba, Sasktchewan and Alberta for over 22 years of observation. Similar results were obtained by Finnell (1935) in Oklahoma soils in U. S. A. The above statement indicates that the land brought under cultivation loses its humus and organically bound nitrogen year after year if they are not supplied with sufficient quantity of organic matters. The alkali soils are very poor in their humus and nitrogen content apart from the fact that they are unfit for cultivation due to high pH and high alkali salt contents. The authors' view to improve the alkali soil was first to improve the humus status and at the same time to raise the nitrogen level by using the carbonaceous materials rich in lignin and polysaccharides with and without rock phosphate. More than thirty years have now passed for Dhar's (1965) new theory of nitrogen fixation in soil. The energy received from the solar system on the earth or produced artificially is as much potential as from any other sources like atomic energy and so on and is distributed in quantum as reviewed earlier. The nitrogen fertility problem is an acute problem of the world especially for the tropical region soils the reduction of carbon of the atmosphere into sugars during the process of photosynthesis utilises light energy as a source as reviewed earlier according to Dhar's theory the release of energy from the oxidation of carbonaceous material as well as the energy obtained from light absorption, both play important role individually and more effectively when two are together. A brief explanation is given as under :

When the carbonaceous materials are added in the soil, they undergo slow oxidation and the carbon of the system decreases and exothermic reaction takes place causing release of energy.

$$H_{12}O_6 + 6 O_2 \rightleftharpoons 6 CO_2 + 6 H_2O + 676 \text{ K. cals.}$$
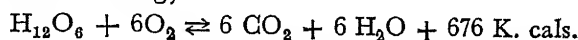
The reaction is accelerated by light radiation energy absorbed in the system. The energy released is utilized in the photolysis of water molecules.

$$H_2O + 112 \text{ K. cals} = H + OH$$
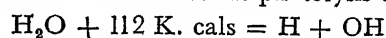
The atomic or nacent hydrogen formed combines with the atmospheric nitrogen on the surface of soil particles or any other surface and nitrogen is fixed.

$$6 H_2O + 672 \text{ K. cals} \rightleftharpoons 6 H + 6 OH$$

$$6 H + N_2 \rightleftharpoons 2 NH_3 + 200 \text{ K. cals.}$$
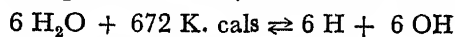
The ammonia formed in this photochemical reaction undergoes further oxidation forming nitrite and nitrates useful for plant growth or combines with carbohydrates forming amino acids and finally into proteins which are retained in the soil. Light energy also helps in the process of oxidation of ammonia into nitrates.

$$NH_3 + O_2 \rightarrow NO_2 \xrightarrow{+O_2} NO_3 + \text{Carbohydrate} \rightarrow \text{aminoacids} \rightarrow \text{proteins},$$ the view is supported by various workers Howard and Wad (1931), Clarke (1930), Meiklejohn (1955), Ranjan and Bhattacharya (1940), Jacks (1939), Kerr (1928), Warmbold (1906) Rossi.

Now the nitrogen fixed by this photochemical process is likely to be lost due to reverse chemical change like denitrification. Phosphate helps to check the nitrogen losses by forming phosphoproteins and other nitrogen phosphorus complexes has also been studied in this investigation.

Methods and Materials

A soil sample of alkali soil collected from Soraon, Allahabad was used for this investigation. The organic materials used were saw dust, molasses (spent wash), wheat straw and Swedish Peat. The sources of phosphates were Bihar and

Trichinopoly rock phosphates. These materials were dried, powdered and passed through a 60 mesh sieve, while molasses was applied as such.

Experimental Procedure

200 g. of soil (air dry) were taken in the enamelled dishes of 24 c.m. diameter. The rates of application of organic materials and phosphates were 1% and 0.25% (P_2O_5) respectively. After mixing them thoroughly in the dishes, moisture was added @ 50% of the moisture holding capacity for 15 days and latter on it was reduced to 25%. Two sets of experiments were conducted, one set exposed to artificial light from a 100 watt electric bulb while the other set was covered with thick black cloth to cut off light. The average room temperature was 28°C.

Composite samples were taken periodically and analysed for organic carbon, total nitrogen, exchangeable calcium, available P_2O_5 and pH. The organic carbon was analysed by Robinson Mclean and Williams' method, total nitrogen by Kjeldahl modified by Treadwell and Hall, exchangeable calcium by Hissink's method, available phosphate as citric acid soluble phosphate. pH was measured by means of glass electrode using Beckman's pH meter.

Experimental Results

Total analysis of soil (Oven dry basis)

Moisture	0·571 %
Loss on ignition	2·630 %
HCl Insoluble	71·402 %
Sesquoxide	14·137 %
Iron oxide	7·744 %
CaO	1·668 %
MgO	0·371 %
K_2O	0·862 %
P_2O_5	0·146 %
Organic carbon	0·137 %
Total nitrogen	0·031 %
pH	10·50 %

Analysis of Organic Material

	Swedish Peat %	Sawdust %	Wheat straw %	Molasses (Spentwash) %
Moisture	14·500	0·187	—	—
Ash	16·780	3·996	—	6·840
SiO_2	5·040	—	—	6·120
P_2O_3	0·340	0·855	—	—
Fe_2O_3	—	0·372	—	—
CaO	5·200	0·773	0·280	1·350
MgO	0·040	0·282	0·060	0·098
K O	0·450	1·150	1·060	0·612
P_2O_5	0·120	0·242	0·053	0·062
Organic carbon	34·560	43·648	38·214	30·920
Total nitrogen	2·460	0·105	0·831	0·56

	Bihar Rock Phosphate %	Trichinopoly Rock Phosphate %
P_2O_5	19·56	27·50
K_2O	3·25	4·50
CaO	11·62	18·75
MgO	0·71	1·92

TABLE 1

200 g. Soil + 1% carbon as Sawdust

Period of exposure in days	Organic carbon %	Total nitrogen %	Carbon oxidised %	Efficiency of nitrogen fixed in mg/g. of C oxidised	Exchangeable Calcium m.e. %	Available P_2O_5 %	pH
			Light				
0	1·1372	0·0336	—	—	3·5	0·032	10·50
60	1·0548	0·0348	0·0824	14·60	4·0	0·042	9·40
120	0·9471	0·0364	0·1901	14·70	4·9	0·048	9·00
180	0·8897	0·0373	0·2481	14·80	5·6	0·056	8·80
280	0·8030	0·0389	0·3342	15·80	5·8	0·063	8·55
			Dark				
0	1·1372	0·0336	—	—	3·5	0·032	10·50
60	1·0729	0·0341	0·0543	9·20	4·0	0 040	9·75
120	0·9668	0·0353	0·1704	9·30	4·5	0·045	9·25
180	0·9416	0·0356	0·1956	10·20	5·2	0·054	8·85
280	0·8671	0·0363	0·2701	10·00	5·4	0·062	8·75

TABLE 2

200 g. Soil + 1% C as Sawdust + 0·25% P_2O_5 as Bihar Rock Phosphate

			Light				
0	1·1372	0·0836	—	—	3·5	0·042	10·50
60	0·9838	0·0372	0·1534	23·50	3·2	0·054	9·05
120	0·8849	0·0400	0·2523	25·40	6·4	0·067	8·80
180	0·8018	0·0420	0·3354	25·00	6·7	0·101	8·50
280	0·6648	0·0458	0·4724	25·90	6·9	0·113	8·00
			Dark				
0	1·1372	0·0336	—	—	3·5	0·042	10·50
60	1·0059	0·0351	0·1303	11·5	4·8	0·046	9·25
120	0·9449	0·0360	0·1913	12·5	5·8	0·055	8·95
180	0·8873	0·0368	0·2499	13·1	6·2	0·094	8·75
280	0·7969	0·0378	0·3403	12·4	6·4	0·110	8·25

TABLE 3

200 g. Soil + 1% carbon as Sawdust + 0·25% P_2O_5 as Trichinopoly Rock Phosphate

Period of exposure in days	Organic carbon %	Total nitrogen %	Carbon oxidised %	Efficiency of nitrogen fixed in mg/g. of C. oxidised	Exchangeable Calcium m.e. %	Available P_2O_5 %	pH
Light							
0	1·1372	0·0336	–	–	3·5	0·042	10·50
60	0·9943	0·0373	0·1429	25·2	4·6	0·054	9·05
120	0·8902	0·0397	0·2470	24·7	6·0	0·075	8·70
180	0·8436	0·0408	0·2936	24·5	6·4	0·098	8·55
280	0·6939	0·0451	0·4423	26·0	6·5	0·120	8·05
Dark							
0	1·1372	0·0336	–	–	3·5	0·042	10·50
60	1·0407	0·0348	0·0965	12·4	4·4	0·048	9·25
120	0·9461	0·0359	0·1911	12·0	4·7	0·057	8·90
180	0·8818	0·0368	0·2553	12·5	5·8	0·079	8·65
280	0·7852	0·0380	0·3520	12·2	6·3	0·105	8·30

TABLE 4

200 g. Soil + 1% Carbon as Molasses (Spent wash)

Period of exposure in days	Organic carbon %	Total nitrogen %	Carbon oxidised %	Efficiency of nitrogen fixed in mg/g. of C. oxidised	Exchangeable Calcium m.e. %	Available P_2O_5 %	pH
Light							
0	1·1372	0·0758	–	–	3·5	0·032	10·50
60	0·8623	0·0824	0·2749	24·4	3·8	0 042	9·80
120	0·6420	0·0886	0·4952	27·9	4·4	0·043	9·25
180	0·4050	0·0952	0·7322	26·5	5·5	0·044	8·55
Dark							
0	1·1372	0·0758	–	–	3·5	0·032	10·50
60	0·8820	0·0800	0·2552	16·4	3·6	0·041	10·05
120	0·6772	0·0838	0·4600	17·4	4·2	0·042	9 50
180	0·4560	0·0880	0·6812	17·9	4·8	0·042	8·75

TABLE 5

200 g. Soil + 1%C as Spentwash + 0·25% P_2O_5 as Bihar Rock Phosphate

Period of exposure in days	Organic carbon %	Total nitrogen %	Carbon oxidised %	Efficiency of nitrogen fixed in mg/g. of C. oxidised	Exchangeable Calcium m.e. %	Available P_2O_5 %	pH
Light							
0	1·1372	0·0758	–	–	3·5	0·042	10·50
60	0·7853	0·0864	0·3519	30·0	4·6	0·048	9·65
120	0·5280	0·0948	0·6092	31·1	5·8	0·060	9·25
180	0·3150	0·1024	0·8222	32·3	6·8	0·082	8·05
Dark							
0	1·1373	0·0758	–	–	3·5	0·042	10·50
60	0·8680	0·0812	0·2692	20·0	4·5	0·045	9·80
120	0·6480	0·0868	0·4892	22·4	5·7	0·048	9·50
180	0·4379	0·0914	0·6993	22·3	6·2	0·071	8·35

TABLE 6

200 g. Soil + 1% C as Spentwash + 0·25% P_2O_5 as Trichinopoly Rock Phosphate

Period of exposure in days	Organic carbon %	Total nitrogen %	Carbon oxidised %	Efficiency of nitrogen fixed in mg/g. of C oxidised	Exchange-able Calcium m.e. %	Avail-able P_2O_5 %	pH
			Light				
0	1·1372	0·0758	–	–	3·5	0·043	10·50
60	0·8230	0·0859	0·3142	32·2	5·5	0·065	9·75
120	0·5810	0·0943	0 5562	33·2	6·6	0·083	8·40
180	0·3405	0·1035	0·7967	34·8	6·8	0·088	8·30
			Dark				
0	1·1372	0·0758	–	–	3·5	0·043	10·50
60	0·8536	0·0812	0·2836	19·0	5·2	0·058	9·80
120	0·6181	0·0864	0·5191	22·4	6·4	0·073	8·80
180	0·4050	0·0903	0·7322	19·7	6·4	0·077	8·40

TABLE 7

200 g. Soil + 1% C as Wheat Straw

Period of exposure in days	Organic carbon %	Total nitrogen %	Carbon oxidised %	Efficiency of nitrogen fixed in mg/g. of C oxidised	Exchange-able Calcium m.e. %	Avail-able P_2O_5 %	pH
			Light				
0	1·1372	0·0445	–	–	3·5	0·032	10·60
60	0·8562	0·0510	0·2810	23·1	4·4	0·047	9·45
120	0·6795	0·0550	0 4577	23·0	5·2	0·056	8·80
180	0·5250	0·0586	0·6012	23·1	5·8	0·068	8·05
			Dark				
0	1·1372	0·0445	–	–	3·5	0·032	10·50
60	0·8892	0·0488	0·2480	17·2	4·3	0·042	9·65
120	0·7652	0·0512	0 3720	18·0	5·0	0·050	9·25
180	0·6750	0·0529	0·4622	18·0	5·4	0·062	8·30

TABLE 8

200 g. Soil + 1% C as Wheat straw + 0·25% P_2O_5 as Bihar Rock Phosphate

Period of exposure in days	Organic carbon %	Total nitrogen %	Carbon oxidised %	Efficiency of nitrogen fixed in mg/g. of C oxidised	Exchange-able Calcium m.e. %	Avail-able P_2O_5 %	pH
			Light				
0	1·1372	0·0445	–	–	3·5	0·042	10·50
60	0·8080	0·0557	0·3392	33·0	4·8	0·075	9·05
120	0·6270	0·0614	0·5102	30·0	5·9	0·088	8·50
180	0 4800	0·0665	0·6572	32·0	6·8	0·099	7·90
			Dark				
0	0·1372	0·0445	–	–	3·5	0·042	10·50
60	0·8570	0 0512	0·2802	24·0	4·5	0·051	9·25
120	0·6916	0·0537	0·4456	24·0	5·2	0·076	8·50
180	0·5700	0·0558	0·5672	20·0	6·2	0·082	8·00

TABLE 9

200 g. Soil + 1% C as Wheat straw + 0·25 % P$_2$O$_5$ as Trichinopoly Rock Phosphate

Period of exposure in days	Organic carbon %	Total nitrogen %	Carbon oxidised %	Efficiency of nitrogen fixed in m/g. of C oxidised	Exchangeable Calcium m.e. %	Available P$_2$O$_5$ %	pH
			Light				
0	1·1372	0·0445	—	—	3·5	0·043	10·50
60	0·8801	0·0538	0·2572	36·2	4·8	0·062	9·05
120	0·6815	0·0609	0·4557	36·0	5·9	0·088	8·50
180	0·4795	0·0668	0·6577	34·0	6·9	0·107	8·00
			Dark				
0	1·1372	0·0445	—	—	3·5	0·043	10·50
60	0·8950	0·0508	0·2422	26·0	4·6	0·060	9·30
120	0·7302	0·0543	0·4070	24·0	5·5	0·082	8·65
180	0·6210	0·0569	0·5162	24·0	6·4	0·098	8·15

TABLE 10

200 g. Soil + 1% C as Swedish Peat

Period	Organic carbon	Total nitrogen	Carbon oxidised	Efficiency	Exchangeable Calcium	Available P$_2$O$_5$	pH
			Light				
0	1·1372	0·1794	—	—	3·5	0·032	10·50
60	1·0068	0·1818	0·1304	14·4	4·0	0·040	9·45
120	0·8627	0·1844	0·2745	18·5	4·2	0·044	9·05
180	0·7254	0·1871	0·4118	18·6	6·4	0·062	8·60
280	0·5682	0·1904	0·5690	19·3	6·5	0·068	8·45
			Dark				
0	1·1372	0·1794	—	—	3·5	0·032	10·50
60	1·0076	0·1810	0·1296	12·3	4·0	0·038	9·55
120	0·8731	0·1827	0·2641	12·6	4·5	0·040	9·05
180	0·8309	0·1832	0·3063	12·5	6·0	0·048	8·85
280	0·7082	0·1852	0·4290	13·5	6·3	0·062	8·45

TABLE 11

200 g. Soil + 1% C as Swedish Peat + 0·25% P$_2$O$_5$ as Bihar Rock Phosphate

Period	Organic carbon	Total nitrogen	Carbon oxidised	Efficiency	Exchangeable Calcium	Available P$_2$O$_5$	pH
			Light				
0	1·1372	0·1794	—	—	3·5	0·042	10·50
60	0·9812	0·1844	0·1562	33·9	4·8	0·050	9·25
120	0·8151	0·1894	0·3221	31·4	5·9	0·055	9·05
180	0·6504	0·1952	0·4868	32·5	7·2	0·074	8·45
280	0·4720	0·2014	0·6602	33·0	7·9	0·102	8·00
			Dark				
0	1·1372	0·1794	—	—	3·5	0·042	10·50
60	1·0032	0·1827	0·1340	24·6	4·5	0·048	9·40
120	0·8605	0·1860	0·2767	24·2	4·7	0·050	9·05
180	0·7820	0·1879	0·3552	24·1	6·6	0·066	8·45
280	0·6373	0·1915	0·4999	24·2	7·2	0·084	8·20

TABLE 12

200 g. Soil + 1% C as Swedish Peat + 0·25% P_2O_5 as Trichinopoly Rock Phosphate

Period of exposure in days	Organic carbon %	Total nitrogen %	Carbon oxidised %	Efficiency of nitrogen fixed in mg/g. of C oxidised	Exchangeable Calcium m.e. %	Available P_2O_5 %	pH
			Light				
0	1·1372	0·1794	—	—	3·5	0·043	10·50
60	0·9728	0·1847	0·1554	34·2	4·7	0·059	9·40
120	0·8213	0·1902	0·3159	34·5	4·8	0·072	9 00
180	0·6462	0·1967	0·4908	34·2	6·0	0·082	8·45
280	0·4942	0·2025	0·6430	35·5	7·8	0·112	8·00
			Dark				
0	1·1372	0·1794	—	—	3·5	0·043	10·50
60	1·0004	0·1827	0·1368	24·2	4·4	0·049	9·25
120	0·6818	0·1854	0 2754	24·2	4·6	0·062	9·05
180	0·7610	0·1885	0·3762	24·2	6·2	0·088	8·50
280	0·6163	0·1917	0·5209	23·5	7·2	0·092	8·20

Discussion

The foregoing results indicate that the fixation of atmospheric nitrogen has taken place in the alkali soil under investigation. The fixation of nitrogen takes place in normal soils by photochemical reactions have been observed by Dhar and coworkers repeatedly. The original nitrogen content was only 0·0336% which increased to 0·0389% when saw dust was used as source of organic matter. Similarly when molasses (spent wash), wheat straw and Swedish peat were used as source of organic matter, the nitrogen increase were 0·0758% to 0·0952% from 0·0445% to 0·0586% and from 0·1794% to 0·1904 respectively in the presence of light. While in the absence of light there is also increase in the total nitrogen status to the extent of 0·0363%, 0·0880%, 0·0529% and 0·1852% respectively, but the increase is less than that observed in the presence of light (Table 1 to 12). The amount of organic matter oxidised in the presence of light is greater than that in the absence of light has also been observed. Likewise the efficiency of nitrogen fixation *i.e.* the amount of nitrogen fixed in milligram per gram of carbon oxidised is greater in the light than in the dark. The rate of oxidation of organic carbon in different organic matter is of the following order in the light as well as in the dark : Molasses (spent wash) > wheat straw > swedish peat > sawdust.

The results also indicate that when rock phosphate is added with different organic matters reported above, the rate of oxidation of organic carbon and efficiency of nitrogen fixation increases still further in the presence of light than in the absence of light. This also indicate that the phosphate play a vital role in the improvement and maintenance of the nitrogen status of the soil. Dhar and Mukherji (1935) showed experimentally the formation of amino acid by exposing to light solution of nitrate and carbohydrate in the presence of titanium oxide as a photocatalyst, which was detactable by paper chromatography by using ninhydrin. And formation of amino acid was further enhanced when phosphate was added in the solution. This shows that by addition of phosphate in the soil the amount of nitrogen fixed forms phosphoproteins or nucleoproteins by combination of proteins and phosphates.

According to Dhar's theory of photochemical fixation of atmospheric nitrogen, oxidation of a gram molecule of glucose $\frac{1\pm\times676}{336}$ grams of nitrogen can be fixed under ideal conditions. In other words, 0·39 g. of nitrogen should be fixed per g. of carbon oxidised if whole of the energy is utilised for production of ammonia. The ammonia formed in this way readily undergoes oxidation to nitrites and finally to nitrate as under :

1. $2NH_3 + 3O_2 = 2HNO_2 + 2H_2O + 153\cdot7$ k. cals.
2. $NH_3 + 2O_2 = HNO_3 + H_2O + 80\cdot9$ k. cals.
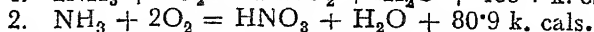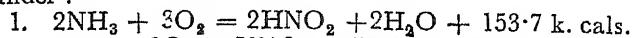
During the process of nitrification there is loss of nitrogen as nitrogen gas due to formation of an unstable substance, ammonium nitrate

$$NH_4NO_2 = N_2 + 2H_2O + 718 \text{ k. cals.}$$
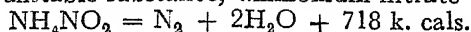
This shows that at least a part of nitrogen fixed is lost as nitrogen gas in the process of nitrification as shown in the above equation. Dhar and Ghosh (1953) reported that loss of nitrogen in the gaseous state can be checked by the addition of alkali salts, where a part of unstable ammonium nitrite may be converted into more stable sodium or potassium nitrite under the present investigation. The alkali soils were already rich in such elements and did not show appreciable loss as ammonium nitrite.

The experimental results show a considerable increase in the amount of exchangeable calcium status of the alkali soils and the increase were of the following order :

Swedish peat > wheat straw > saw dust > spent wash (molasses). And these values increased from 3·5 m.e.% to 6·4 m.e.%, 5·8 m.e.%, 5·6 m.e.% and 5·5 m.e.% respectively. Similar results were obtained in the soils treated with rock phosphate in the presence as well as in the absence of light.

The results recorded indicate a considerable increase in the available phosphate status and lowering of pH values with all types of organic matters used. The original available P_2O_5 was 0·032 % which increased 0·05 or more by the addition of organic matter alone and with the addition of rock phosphate, the value increase to 0·1% or even more. Similarly the pH value decreased to 8·0 which is a remarkable change.

The above investigation makes it clear that the incorporation of organic matter alone. and in combination with the rock phosphate reclaims the highly alkaline soils. Photochemical fixation of atmospheric nitrogen takes place in highly alkali soils where carbon nitrogen balance is restored by increasing the humus and the status of total nitrogen which is very low in the soils under study.

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Influence of Coal in the Improvement of Soil Fertility and Crop Production when Incorporated with Straw and Basic Slag

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Abstract

Powdered coal at the rate of 2·5 tons per acre, wheat straw at the rate of 10 tons per acre were applied in soils with or without phosphates in the form of Tata Basic slag (Thomas slag) and German basic slag at the rate of 50 lbs P_2O_5 per acre in a field trial conducted at Fatuha (Allahabad U. P.). A usual crop rotation (Paddy–wheat–paddy) was taken. It was observed that coal being a less readily oxidisable organic material was slowly activated, when incorporated with wheat straw and basic slags in first year of application.

It was found that the 2nd and 3rd succeeding crops fetched more yields than the first crop due to higher residual effect of coal. The oxidation of coal was enhanced by addition of wheat straw and basic slags.

Introduction

The byproducts of coal industry *i.e.* Ammonium salts were first produced in England in 1840 and were used for many years to increase crop yields. But coal as manure has not been utilized so far.

Coal is vegetable matter that through long geological processes has suffered changes in physical and chemical properties. As coal is derived from organic substances, in order to understand its function as a manure it is necessary to explain the part played by organic materials like farmyard manure, cowdung, leaves, straw etc., in improving crop production. Dhar[1] has emphasised that when organic materials like carbohydrates, lignins, fats, coal etc. are applied without composting, *i.e.* directly to the soil prove more beneficial to crops than the composts obtained from the same materials.

When peat, lignite or bituminous coal is mixed with soil in powdered form, is oxidised slowly and helps in nitrogen fixation. This nitrogen fixation is greatly enhanced when these are mixed with basic slag or finely divided soft rock phosphate.

Dhar and Srivastava[2] concluded that coal mixed with phosphated organic matter when added to the soil is much better for the yield of crop rather than unphosphated organic matter. Dhar and Agarwal[3], have reported that when carbonaceous matter like coal is added along with nitrogenous compounds to the soil, the loss of nitrogen is retarded. Similarly Daniels and Duffie[4] reported that spreading coal dust helps in the retardation of nitrogen loss. Widerhold and Ehrenberg 1923[5], brought ammonia containing gases into contact with the disintergrated lignite, bitumious coal or other carbonaceous materials and used these products as fertilizers. Dhar and coworkers[6], have definitely shown

that peat, lignite and bituminous coal without being ammoniated, when mixed with soil in very finely devided condition, not only add nitrogen they contain but also fix atmospheric nitrogen more in light than in dark.

Further experiments on this problem have been conducted. The influence and residual effect of coal, mixed with organic matter like wheat straw in presence and absence of German basic slag and blue green alga namely Anabaena naviculoides·on the yield of paddy and wheat crops in the field have been studied.

Experimental

Field trials were conducted at Village Fatuha, Allahabad in an area where land is fairly uniform and which is under cultivation since a long time. The structure of soil is sandy loam. Soil samples were taken out from different layers and from different spots upto the depth of 6 inches in order to determine the uniformity of the soil of the field. They were analysed for their consistents. Coal dust and wheat straw were incorporated with and without phosphate to the field two months before transplating of the paddy seedlings, for their complete decomposition. Paddy was transplanted on 28-7-1965 in puddled field and before transplantation wherever necessary the plots were inoculated with Anabaena naviculoids. Before sowing and after harvesting of each crop soil samples were taken from each plot and complete analysis was made.

Design of Experiment	*Randomised block design*
Number of treatments	14
Number of replication	4
Total No. of plots.	56
Area and size of the plot	1/69th of an acre

Rate of addition of the amendments/acre

Organic matter	10 tons
Coal dust	$2\frac{1}{2}$ tons
Phosphate (G. B. S.).	50 lbs P_2O_5

Treatments

1. Soil alone
2. Soil + Coal
3. Soil + W. S.
4. Soil + G. B. S.
5. Soil + Coal + W. S.
6. Soil + G. B. S. + Coal.
7. Soil + G. B. S. + W. S.
8. Soil + W. S. + Coal + G. B. S.
9. Soil + Anabaena
10. Soil + Anabaena + Coal
11. Soil + W. S. + Anabaena
12. Soil + G. B. S. + Coal + Anabaena
13. Soil + W. S. + G. B. S. + Anabaena
14. Soil + W. S. + G. B. S. + Coal + Anabaena

Note:— G. B. S. = German basic slag.
W. S. = Wheat Straw.

TABLE 1
Analysis of materials used in field trials %

Estimation	Soil	Coal	G.B.S.	W.S.
Loss on ignition	4·3617	89·3857	–	89·8530
Ash	94·4385	10·1854	–	8·8526
HCl (insoluble)	80·4926	6·0163	12·1056	5·0384
Sesquioxide	10·9715	1·5682	–	1·3625
Fe_2O_3	3·3627	0·8297	15·014	0·6174
Total P_2O_5	0·1275	0·2935	17·396	0·53·04
Available P_2O_5	0·0165	–	9·6365	–
CaO	1·2364	1·3845	42·0250	0·7538
MgO	0·4884	1·4156	4·9750	0·1807
K_2O	0·8743	0·8704	Traces	0·6025
Total carbon	0·4863	73·5936	–	38·2165
Total Nitrogen	0·0462	1·2128	–	0·6295
NH_3–––N	0·0019	–	–	–
NO_3–––N	0·0032	–	–	–
C/N ratio				
pH	7·6			

TABLE 2

Average yield of grain and straw in Kgs per plot (1/60th acre)

(Average of four plots)

Treatments	Paddy		Wheat	
	grain (Kgs)	straw (Kgs)	grain (Kgs)	straw (Kgs)
Soil alone	9·0	16·0	8·5	16·2
Soil + Coal	9·9	17·4	9·6	17·5
Soil + W.S.	13·4	23·6	12·5	22·7
Soil + G.B.S.	10·8	18·6	9·9	18·1
Soil + Coal + W.S.	14·4	25·1	13·6	24·3
Soil + G.B.S. + Coal	11·7	20·6	10·8	19·7
Soil + G.B.S. + W.S.	16·7	27·7	16·3	30·8
Soil + W.S. + Coal + G.B.S.	17·9	30·1	17·4	32·5
Soil + Anabaena	10·0	17·5	8·8	16·5
Soil + Coal + Anabaena	10·8	18·7	9·7	18·0
Soil + W.S. + Anabaena	14·6	25·3	12·8	23·1
Soil + G.B.S. + Coal + Anabaena	12·8	22·5	11·1	16·9
Soil + W.S. + G.B.S. + Anabaena	18·0	29·9	16·7	31·2
Soil + Coal + W.S. + G.B.S. + Anabaena	19·3	31·7	17·8	32·0

TABLE 3

Analysis of soil samples before transplantation of paddy (Percentage)

Treatments	Total carbon	Total nitrogen	NH—$_3$N	NO$_3$—N	Total P$_2$O$_5$	Avail. P$_2$O$_5$
Soil alone	0·4863	0·0462	0·0019	0·0032	0·1275	0·0165
Soil + Coal	0·6958	0·0527	0·0020	0·0034	0·1276	0·0167
Soil + W.S.	0·6825	0·0670	0·0032	0·005?	0·1357	0·0215
Soil + G.B.S.	0·4805	0·0471	0·0023	0·0037	0·1446	0·0327
Soil + Coal + W.S.	0·9857	0·0725	0·0035	0·0056	0·1359	0·0219
Soil + G.B.S. + Coal	0·6875	0·0529	0·0024	0·0039	0·1448	0·0328
Soil + W.S. + G.B.S.	0·6257	0·0753	0·0053	0·0076	0·1729	0·0507
Soil + W.S. + G.B.S. + Coal	0·9208	0·0829	0·0055	0·0079	0·1730	0·0508
Soil + Anabaena	0·4865	0·0464	0·0021	0·0035	0·1276	0·0165
Soil + Coal + Anabaena	0·6959	0·0529	0·0022	0·0035	0·1277	0·0168
Soil + W.S. + Anabaena	0·6827	0·0675	0·0034	0·0055	0·1357	0·0217
Soil + G.B.S. + Coal + Anabaena	0·6876	0·0530	0·0026	0·0040	0·1449	0·0330
Soil + W.S. + G.B.S. + Anabaena	0·6259	0·0755	0 0055	0·0077	0·1729	0·0509
Soil + Coal + W.S.+ G.B.S. + Anabaena	0·9210	0·0830	0·0057	0·0082	0·1733	0·0510

TABLE 4

Analysis of soil samples after harvest of paddy crop (Percentage)

Treatments	Total carbon	Total nitrogen	NH$_3$—N	NO$_3$—N	Total P$_2$O$_5$	Avail. P$_2$O$_5$
Soil alone	0·4795	0·0458	0·0017	0·0030	0·1271	0·0160
Soil + Coal	0·6897	0·0521	0·0018	0·0032	0·1272	0 0165
Soil + W.S.	0·5928	0·0648	0·0027	0·0047	0·1315	0·0257
Soil + G.B.S.	0·4750	0·0462	0·0020	0·0034	0·1408	0 0403
Soil + Coal + W.S.	0·8795	0·0690	0·0030	0·0052	0·1317	0·0261
Soil + G.B.S. + Coal	0·6801	0·0423	0·0019	0·0034	0·1407	0·0410
Soil + W.S. + G.B.S.	0·5713	0·0702	0 0041	0·0064	0·1658	0 0586
Soil + W.S. + G.B.S. + Coal	0·3574	0·0765	0·0043	0 0068	0·1659	0·0589
Soil + Anabaena	0·4797	0·0459	0·0018	0·0032	0·1270	0·0162
Soil + Coal + Anabaena	0·5839	0·0523	0 0019	0·0033	0·1273	0·0167
Soil + W.S. + Anabaena	0·5927	0·0650	0·0028	0·0049	0·1314	0·0260
Soil + G.B.S. + Coal + Anabaena	0·6800	0·0525	0·0021	0·0036	0·1405	0·0413
Soil + W.S. + G.B.S. + Anabaena	0·5715	0·0703	0·0042	0·0065	0·1657	0·0597
Soil + Coal + W.S.+ G.B.S. + Anabaena	0·8576	0·0767	0·0045	0·0069	0·1658	0·0593

TABLE 5
Analysis of soil samples after harvest of wheat crop (Percentage)

Treatments	Total carbon	Total nitrogen	NH₃—N	NO₃—N	Total P₂O₅	Avail. P₂O₅
Soil alone	0·4732	0·0451	0·0015	0·0023	0·1269	0·0153
Soil + Coal	0·6802	0·0519	0·0017	0·0030	0·1270	0·0155
Soil + W.S.	0·5419	0·0607	0·0025	0·0041	0·1302	0·0239
Soil + G.B.S.	0·4653	0·0459	0·0019	0·0032	0·1397	0·0387
Soil + Coal + W.S.	0·4895	0·0647	0·0028	0·0048	0·1304	0·0245
Soil + G.B.S. + Coal	0·6758	0·0520	0·0018	0·0031	0·1395	0·0389
Soil + W.S. + G.B.S.	0·5287	0·0673	0 0037	0 0055	0·1584	0·0576
Soil + W.S. + G.B.S. + Coal	0·8039	0 0728	0·0039	0·0057	0·1587	0·0579
Soil + Anabaena	0·4734	0·0452	0·0015	0·0029	0·1268	0·0154
Soil+Coal+Anabaena	0 6804	0·0520	0·0018	0·0030	0·1269	0·0157
Soil+W.S.+Anabaena	0·5120	0·0608	0·0026	0·0041	0·1301	0·0240
Soil + G.B.S. + Coal + Anabaena	0·6759	0·0521	0·0019	0·0032	0·1394	0·0390
Soil + W.S.+G.B.S. + Anabaena	0·5289	0·0675	0·0038	0·0057	0·1583	0·0578
Soil + Coal + W.S.+ G.B.S. + Anabaena	0 8040	0·0729	0·0039	0·0059	0·1586	0 0580

Discussion

A careful examination of the results recorded in yield table No. 2 shows that there is increase in the yield of paddy and wheat crops, in coal treated plot. When coal was incorporated with phosphated organic matter, much better results were obtained than the treatments in which only coal, organic matter and algae alone was added. Following table shows an increase in the yield due to various treatments over control.

Average yield of paddy grain 9 Kgs and wheat grain 8·5 Kgs in control plot.

TABLE 6

S. N.	Treatments	Increase in paddy grain in Kg.	Increase in wheat grain in Kg.
1.	Soil + Coal	0·9	1 1
2.	Soil + W. S.	4·4	4·0
3.	Soil + G. B. S.	1·8	1·4
4.	Soil + Coal + W. S.	5·4	5·1
5.	Soil + G. B. S. + Coal	2·7	2·3
6.	Soil + G. B. S. + W. S.	7·7	7·8
7.	Soil + W. S. + Coal + G. B. S.	8·9	8·9
8.	Soil + Anabaena	1·0	0·3
9.	Soil + Coal + Anabaena	1·8	1·2
10.	Soil + W. S. + Anabaena	5·6	4·3
11.	Soil + G. B. S. + Anabaena + Coal	3·8	2·6
12.	Soil + W. S. + G. B. S. + Anabaena	9·0	8·8
13.	Soil + W. S. + Coal + G. B. S + Anabaena	10·3	9·3

It is interesting to note that increase in yield of paddy and wheat grain due to addition of coal is only 0·9 Kg and 1·1 Kg and due to inoculation of algae is 1·0 Kg. and 0·3 Kg respectively. This increase in yield of wheat grains in case of coal addition is due to its residual effect because it oxidizes very slowly.

Influence of coal in production of paddy crop is not much but when applied with organic matter and phosphate there is marked increase in yield of crop.

The value of coal as manure is not only due to the nitrogen it contains, but it is its nitrogen fixing power and contents of minerals that increase its usefulness as a manure in improving crop production. Proul (1921) 7, of Indiana Experimental Station has determined the relative crop production value of muck and sodium nitrate when applied to corn on equivalent nitrogen basis. He proved that muck and other organic manures have much more residual effect than sodium ntrate and thus benefit succeeding crops and improve soil tilth and crumb formation and water retention capacity by increasing the humus capital of the soil.

From the yield table No. 2 it has also been observed that the phosphated coal or organic matter mixed with soil is better than unphosphated organic matter. Dhar, Ghildayal and others⁶ carried out field trials and found bituminous coal very favourable for growing both paddy and wheat crops.

It is concluded that the addition of phosphated organic matter specially coal mixed phosphated organic matter rather than coal alone or unphosphated organic matter to the soil, is much better in improvement of crop production. It has been also concluded that coal being less oxidizable organic matter is beneficial to succeeding crops due to its residual effect ; oxidation of coal is enhanced by the addition of wheat straw and basic slags.

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Effect of Basic Slags on the Slow and Induced Oxidation of Energy Material (Sucrose)

By

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Abstract

It has been observed that the slow and induced oxidation of sucrose is greatly enhanced by the presence of basic slags. The capacity of different slags to enhance these oxidations varies with the P_2O_5 content of the basic slag. As these oxidations proceed the pH of the medium falls sharply in the beginning and slowly at the later stages. But in the illuminated sets as the pH approaches neutrality it again starts rising up though slowly. The amount of carbon dioxide actually liberated is invariably found to be lower than the theoretical value of CO_2 corresponding to the amount of carbon lost during the oxidation. The oxidation is found to be much greater in light than in dark.

Introduction

The importance of phosphatic fertilizers has been greatly emphasised during recent years. The basic slag a bye product of the steel industry is a cheap and abundant source of P_2O_5. Wagner[1] in 1884 showed that the powdered basic slag had a striking effect on the crops specially of the leguminous order. Russell[2], Cullen[3], Noll, Irwin and Gardener[4] have shown the superiority of basic slags over superphosphate and bone meal. Whittaker[5] obtained marked beneficial effects on the plant growth. Similar results were obtained by Williams and Custon[6].

In recent years Dhar and co-workers have pioneered the study of Indian basic slags as fertilizer. In a number of recent publications[7-12] they have shown that the basic slag not only acts as a phosphorus nutrient to the plant body but also help the fixation of nitrogen. They have further shown that the basic slag can also be helpful in reclamation of alkali soils. Williams[13] and Skinner[14] also concluded that not only phosphates but a mixture of phosphate and organic matter can be better proposition. Charlon[15] concludes that due to constant use of basic slag the increase in growth is not merely transient but constitutes a permanent advantage.

Dhar[16] pointed out that cellulosic substances as also sugars constantly undergo oxidation, which can be represented as below :

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + 767 \text{ K. Cal.}$$
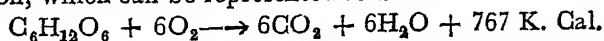
The energy so liberated is utilized in accomplishing the photolysis of water :

$$H_2O + 112 \text{ K. Cal.} \longrightarrow H + OH.$$
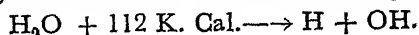
The chemical combination between atmospheric nitrogen and atomic hydrogen obtained by the photolysis of water leads to the formation of ammonia :

$$N_2 + 6H \longrightarrow 2NH_3.$$

[393]
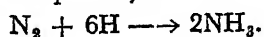
This ammonia in turn is oxidised to form nitrite and nitrate and thus atmospheric nitrogen is fixed.

Thus it is evident that the oxidation of organic matter is one of the chief factors which govern the fixation of nitrogen from atmosphere. Keeping this fact in view the study of the factors influencing the slow oxidation of organic matter is of very much importance.

The aim of the present work is to study the exclusive effect of Tata, German and Belgian basic slags on the slow and induced oxidation of organic matter (sucrose has been taken here) and its subsequent effect on the system.

Experimental

100 ml of 1·5% solution of sucrose (B. D. H., A. R.) was taken separately in two conical flasks of 350 ml capacity. In another 100 ml of the same sugar solution the amount of organic carbon was determined by the method of Robinson, Mclean and Williams[17]. To these flasks 0·0225 gm of Fe^{++} was added in the form of ferous hydroxide inductor which was freshly precipitated almost in a neutral medium in an atmosphere of nitrogen gas, from a solution of ferous sulphate (B. D. H., A. R.). Then 1 gm of powdered, 100 mesh sieved, Tata or German or Belgian basic slag was also added to each of the flasks. A crystal of Mercuric chloride was also added to these flasks in order to check the growth of microorganisms. The flasks were then shaken well for 10 minutes in a corked position and fitted in a specially designed leakage proof system and kept in a thermostat at 30°C. One of the flasks was well covered with a thick black cloth in order to eliminate the influence of light on its contents. The other flask was kept exposed to a 200 watt bulb light kept at a distance of 3 feet. Measured and equal volumes of bacteria and Carbondioxide free air was passed through the solutions in the flasks slowly in a fixed time. Every time fresh sets were taken. The flasks were shaken after every 30 minutes. The gas mixture escaping from the flasks was conducted separately through Pettenkoffer tubes containing standard baryta solution which absorbed the CO_2 from the gas mixture. The distant ends of the Pettenkoffer tubes was attached to soda-lime guard tubes. Finally the contents of the flasks were filtered and the filtrate along with the washings was estimated for organic carbon.

The contents of the Pettenkoffer tubes were filtered in a CO_2 free chamber and then remaining baryta was estimated by titration against standard HCl[18]. From this the amount of CO_2 liberated by the oxidation of the sugar was calculated. The whole process was repeated after adding 2, 3 or 4 gms of the said basic slags. The pH of the system was also measured both at the beginning and the end of the experiment by a portable Cambridge pH meter.

Results

Table showing percentage of Metal Oxides and P_2O_5 in Basic Slags

Contents	Tata Basic Slag	German Basic Slag	Belgian Basic Slag
SiO_2	15·5298	12·0928	12·2562
Fe_2O_3	4·0000	4·2536	5·1280
FeO	10·5219	8·0138	8·5226
Al_2O_3	5·5201	3·1298	3·0544
CaO	38·8964	42·5282	42·0026
MgO	4·6647	4·8587	4·5683
K_2O	0·6519	Traces	Traces
V_2O_5	0·5265	0·6918	0·5585
Cr_2O_3	1·40198	0·4888	0·4001
TiO_2	0·3029	0·5015	0·2536
CuO	0·0050	0·0051	0·0090
ZnO	0·0071	0·0057	0·0067
P_2O_5	7·8058	18·0562	16·7654
MnO	2·8951	4·7256	4·1267

Discussion

A perusal of the foregoing results reveals that the slow and induced oxidation of sucrose is greatly enhanced by the presence of basic slags and that the capacity of the different basic slags to enhance these oxidations varies with the P_2O_5 content of the slag. Harden and Young[19] demonstrated that the sugars glucose, fructose and mannose must pass through an intermediate stage of combination with phosphoric acid before they are broken down. Embden and Zimmermann[20], Pryde and Waters[21] Meyerhof[22] and many others have also obtained results which confirm the above view.

It appears that the sucrose molecule is first broken into hexoses. These hexose molecules combine with the Phosphoric acid which is being generated in the solution due to the presence of the basic slag and form an intermediate hexose phosphate. This intermediate compound acts as a precurser for the further breaking down of the sugar. Therefore the more the phosphoric acid is available, the more of this intermediate phosphate is formed and hence more of sugar is oxidised. Moreover, due to carbonic acid and other organic acids being formed during the course of oxidation more of P_2O_5 must be coming to the solution and hence more of phosphate ions are rendered available. Gupta[23] Pant[24] and Kapoor[25] showed that the solubility of basic slag is increased in dilute solutions of organic acids. Our results also confirm the views of Lob and co-workers[26-27] that the phosphates exert a specific accelerating effect on the oxidation of glucose. Witzemann also supports this view[28]. However, Harden and Henley[29] consider that the action of phosphates is not specific but depends on their capacity to act as buffers.

Table Showing Effect of Basic Slags on the Slow and Induced Oxidation of Sucrose

T.B.S.=Tata Basic Slag,　G.B.S.=German Basic Slag,　B.B.S.=Balgian Basic Slag

Vol. of air passed (lts.)	Time for passing air (Hrs.)	Sugar oxidised in terms of carbon %	CO_2 Corresponding to carbon oxidised gm.	CO_2 Liberated gm.	Final pH	Sugar oxidised in terms of carbon %	CO_2 Corresponding to carbon oxidised gm.	CO_2 Liberated gm.	Final pH

1·5 gm. Sucrose + 0·0225 gm. Fe++ as Fe (OH)₂.　Initial pH = 7·55

		Light				*Dark*			
30	25	2·12	0·0525	0·05102	7·50	–	–	–	7·55
60	50	2·79	0·0644	0·0612	7·50	1·49	0·0346	0·0301	7·50
90	75	3·24	0·0748	0·0720	7·40	1·75	0·0404	0·0382	7·45
120	100	3·60	0·0831	0·0800	7·35	1·92	0·0442	0·4019	7·45
150	125	3·98	0·0918	0·8812	7·30	2·01	0·0462	0·4125	7·40

1·5 gm. Sucrose + 1·00 gm. T.B.S. + 0·0225 gm Fe++ as Fe (OH)₂.

Initial pH = 2·95

30	25	14·84	0·3426	0·2914	8·50	6·78	0·1565	0·1246	8·60
60	50	22·16	0·5116	0·4364	8·05	9·99	0·2305	0·1852	8·35
90	75	26·74	0·6174	0·5162	7·50	12·62	0·2918	0·2345	8·10
120	100	28·35	0·6546	0·5291	7·25	13·55	0·3128	0·2499	8·00
150	125	30·29	0·6993	0·5539	7·45	14·28	0·3187	0·2501	7·85

1·5 gm. Sucrose + 2·00 gm. T.B.S. + 0·0225 gm. Fe++ as Fe (OH)₂

Initial pH = 9·25

30	25	18·45	0·4260	0·3608	8·60	8·05	0·1858	0·1478	8·80
60	50	26·22	0·6054	0·5202	8·10	11·12	0·2566	0·1967	8·40
90	75	30·00	0·6927	0·5860	7·45	14·36	0·3315	0·2518	8·10
120	100	32·16	0·7425	0·6178	7·20	16·00	0·3694	0·2721	7·80
150	125	37·05	0·8554	0·7226	7·50	17·50	0·4040	0·2996	7·65

1·5 gm. Sucrose + 3·00 gm. T.B.S. + 0·0225 gm. Fe++ as Fe (OH)₂.

Initial pH = 9·55

30	25	22·82	0·5268	0·4466	8·85	10·08	0·2327	0·1894	9·15
60	50	30·51	0·7044	0·5738	8·10	13·96	0·3223	0·2718	8·85
90	75	34·26	0·7910	0·6382	7·45	16·25	0·3752	0·3164	8·50
120	100	40·00	0·9236	0·7533	7·55	18·86	0·4354	0·3724	8·30
150	125	47·99	1·1081	0·9128	7·75	20·51	0·4042	0·4042	8·10

Vol. of air passed (lts.)	Time for passing air (Hrs.)	Sugar oxidised in terms of carbon %	CO$_2$ corresponding to carbon oxidised gm.	CO$_2$ Liberated gm.	Final pH	Sugar oxidised in terms of carbon %	CO$_2$ corresponding to carbon oxidised gm.	CO$_2$ Liberated gm.	Final pH

1·5 gm. Sucrose + 4·00 gm. T.B.S. + 0·0225 gm. Fe^{++} as Fe (OH)$_2$.

Initial pH = 9·55

		Light				*Dark*			
30	25	25·52	0·5892	0·4723	8·75	12·78	0·2944	0·2423	9·00
60	50	36·22	0·8330	0·6687	7·95	16·65	0·3844	0·2917	8·55
90	75	39·54	0·9129	0·7237	7·35	20·00	0·4618	0·3588	8·05
120	100	44·98	1·0385	0·8189	7·55	23·18	0·5352	0·4008	7·75
150	125	55·10	1·2716	0·9748	7·75	25·57	0·5904	0·4275	7·55

1·5 gm. Sucrose + 1·00 gm. G.B.S. + 0·0225 gm. Fe^{++} as Fe (OH)$_2$.

Initial pH = 8·60

30	25	20·20	0·4664	0·4021	8·00	9·00	0·2078	0·1722	8·25
60	50	27·81	0·6421	0·5512	7·55	12·58	0·2304	0·2361	7·95
90	75	32·02	0·7393	0·6257	7·20	15·65	0·3615	0·3001	7·70
120	100	34·16	0·7887	0·6392	7·35	17·56	0·4054	0·3320	7·45
150	125	39·38	0·9092	0·7546	7·55	19·37	0·4472	0·3826	7·25

1·5 gm. Sucrose + 2·00 gm. G.B.S. + 0·0225 gm. Fe^{++} as Fe (OH)$_2$.

Initial pH = 8·85

30	25	24·52	0·5661	0·5017	8·20	11·82	0·2739	0·2301	8·40
60	50	34·68	0·8007	0·7052	7·65	15·57	0·3595	0·2913	8·05
90	75	39·16	0·9042	0·7720	7·25	18·62	0·4298	0·3500	7·75
120	100	42·22	1·0408	0·8931	7·45	20·91	0·4828	0·8902	7·50
125	125	48·35	1·1164	0·9502	7·60	23·34	0·5399	0·4218	7·35

1·5 gm. Sucrose + 3·00 gm. G.B.S. + 0·0225 gm. Fe^{++} as Fe (OH)$_2$.

Initial pH = 8·90

30	25	29·18	0·6787	0·6125	8·20	13·87	0·3202	0·2715	8·55
60	50	37·56	0·8672	0·7784	7·65	17·29	0·3992	0·3326	8·05
90	75	42·75	0·9871	0·8675	7·25	19·55	0·4514	0·3701	7·60
120	100	48·95	1·1292	0·9728	7·55	22·41	0·5175	0·4062	7·30
150	125	55·46	1·2805	1·1123	7·80	25·87	9·5973	0·4682	7·10

1·5 gm. Sucrose + 4·00 gm. G.B.S. + 0·0225 gm. Fe^{++} as Fe (OH)$_2$.

Initial pH = 9·00

30	25	35·45	0·8185	0·7402	8·35	15·02	0·3468	0·2915	8·55
60	50	42·08	0·9716	0·8632	7·75	19·48	0·4497	0·3728	8·05
90	75	46·00	0·2621	0·9315	7·30	22·35	0·5160	0·4235	7·65
120	100	61·98	1·2002	0·0400	7·50	24·02	0·5546	0·4327	7·30
150	125	62·55	1·4443	0·2651	7·75	27·99	0·6462	0·5239	7·10

Vol. of air passed (lts.)	Time for passing air (Hrs.)	Sugar oxidised in terms of carbon %	CO_2 corresponding to carbon oxidised gm.	CO_2 Liberated gm.	Final pH	Sugar oxidised in terms of carbon %	CO_2 corresponding to carbon oxidised gm.	CO_2 Liberated gm.	Final pH

1.5 gm. Sucrose + 1.00 gm. B.B.S. + 0.0225 gm. Fe^{++} as Fe (OH)$_2$.

Initial pH = 8.80

		Light					*Dark*		
30	25	16.59	0.3137	0.2612	8.30	8.07	0.1863	0.1425	8.45
60	50	25.06	0.5786	0.3875	7.85	12.06	0.2784	0.2217	8.10
90	75	30.11	0.6952	0.5718	7.55	15.00	0.3563	0.2909	7.95
120	100	33.28	0.7683	0.6279	7.35	16.93	0.3908	0.3114	7.80
150	125	36.02	0.8317	0.6826	7.20	18.21	0.4204	0.3320	7.70

1.5 gm. Sucrose + 2.00 gm. B.B.S. + 0.0225 gm. Fe^{++} as Fe (OH)$_2$.

Initial pH = 9.35

30	25	22.14	0.5112	0.4437	8.65	10.05	0.2320	0.1900	8.90
60	50	31.52	0.7277	0.6084	8.10	14.12	0.3260	0.2685	8.80
90	75	35.24	0.8136	0.6926	7.60	17.53	0.4047	0.3302	8.40
120	100	38.05	0.8639	0.7209	7.25	19.14	0.4419	0.3517	8.10
150	125	42.82	0.9872	0.8123	7.40	20.50	0.4733	0.3064	7.90

1.5 gm. Sucrose + 3.00 gm. B.B.S. + 0.0225 gm. Fe^{++} as Fe (OH)$_2$.

Initial pH = 9.45

30	25	25.84	0.5918	0.5202	8.70	12.24	0.2826	0.2808	9.00
60	50	36.17	0.7351	0.4905	8.15	16.82	0.3883	0.3127	8.55
90	75	40.51	0.9353	0.8056	7.60	20.37	0.4703	0.3920	8.15
120	100	44.67	1.0303	0.8729	7.20	21.50	0.4964	0.4011	7.90
150	125	52.12	1.2034	1.1237	7.45	22.55	0.5206	0.4224	7.75

1.5 gm. Sucrose + 4.00 gm. B.B.S. + 0.0225 gm. Fe^{++} as Fe (OH)$_2$.

Initial pH = 9.55

30	25	29.72	0.6862	0.5231	8.25	14.34	0.3311	0.2701	9.00
50	50	40.45	0.9339	0.8426	8.25	19.91	0.4460	0.3482	8.40
90	75	44.01	1.0194	0.9921	7.60	23.25	0.5364	0.4301	8.15
120	100	50.31	1.1616	1.0035	7.30	25.12	0.5799	0.4806	7.90
150	125	59.41	1.3718	1.1927	7.50	26.22	0.6054	0.4806	7.65

The enhancement of the oxidation in presence of basic slags may also partially be due to the pH of the system being on the alkaline side as indicated by Dhar and Palit[30].

It has also been observed that the pH of the system falls sharply in the beginning but slowly at later stages. At the same time the amount CO_2 caught by the baryta in the Pettenkoffer tubes is always found to be lower than the amount of CO_2 corresponding to the carbon lost from the sugar solution. It is evident that all the CO_2 which is being generated as a result of the oxidation of the sucrose is not being released but a considerable portion of it is being absorbed by the reaction mixture. This absorbed carbonic acid is probably combining with the calcium ions present in the solution and forming insoluble $CaCO_3$. At the same time more of phosphoric acid is entering into the solution. This addition of acid and removal of base must cause a fall in the pH. Further during the oxidation of the sugar many intermediate organic acids would be formed which must cause a further fall in pH.

Kappanna[31] showed that the rate of oxidation of carbohydrates depends a great deal on the pH and lower the pH lower will be the oxidation. Our results also show a similar trend and as the pH falls the rate of oxidation also falls. Due to the fall in the rate of oxidation lesser amount of carbonic acid and other organic acids will be formed and that is why the fall in the pH becomes slow at later stages.

Moreover as the pH approaches neutrality it again shows a slow rise. This appears to be due to the solid $CaCO_3$ getting converted into soluble calciumbicarbonate due to CO_2 being in excess and hence more of Ca ions entering the solution.

The oxidation is found to be much more in illuminated sets than in dark. Dhar and Bhattacharya[32] showed that the light absorption by the reaction mixtures (i) Glucose + H_2O_2 and (ii) in hydrolysis of sucrose is greater than the reactants separately. This increased light absorption appears to be due to activation of the moleculs by the presence of the molecules of other substances. The activation of molecules is associated with the weakening of their binding forces and consequent increased light absorption. This activation must be accelerating the oxidation. Dhar and Bhattacharya[32] also showed that the reactions with greater velocity show greater light absorption. Also the presence of photosensitisers like titania in the basic slag must be playing a role in this respect. All these factors operating together must greatly enhance the oxidation of sucrose in light. The difference in the percentage of oxidation in light and dark is smaller in the case of Belgian basic slag. It is likely to be due to lower titania percentage in the Belgian slag.

The capacity of basic slags to enhance the induced oxidation of sucrose is in the following order :

Tata basic slag < Belgian basic slag < German basic slag.

The foregoing results also show that the Tata basic slag although poorer in P_2O_5 can help the oxidation of energy material to a great extent and hence can help fixation of nitrogen through photolysis of water considerably. Further the basic slag in combination with organic matter can be used as a means for reclaiming alkali soils permanently.

The work in this direction is still continued.

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Influence of Organic matter and Phosphate inoculated with blue green algae (Anabaena naviculoides) and green algae (Chlorella pyrenoidosa) on the reclamation of alkali soils in the presence and absence of light

By

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Abstract

The efficiency of the process of reclamation of alkali soils with a mixture of organic matter and calcium phosphates is increased to a greater extent when inoculated with blue green algae (Anabaena naviculoides) and to a smaller extent when inoculated with green algae (Chlorella pyrenoidosa) and that these algae are not markedly effective when applied alone to alkali soils. No growth of these algae is observed in the dark.

Algae have been intimately connected with human beings from times immemorial. They have been used as food, fodder and as manure. The important application of blue green algae in agriculture in raising the fertility of soil has been recognised only during the past half a century. Some of the blue green algae of the family Nostocaceae, including members of the genera Nostoc, Anabaena Cylindrospermum, and Microchaetaceae, along with members of the genus Aulosira have been shown to prossess the power of fixing nitrogen from the atmosphere[1] and thus have simpler food requirements than any other organisms, since they can obtain both their carbon and nitrogen from the air. Venkataraman and Dutta[2] proved that many blue green algae are capable of fixing atmospheric nitrogen. The dominance of blue green algae, possessing the ability for nitrogen fixation particularly in the tropics, suggests that these organisms are of considerable importance in maintaining soil fertility.

According to Singh[3], these algae can be used in the reclamation of Usar lands. Various species of Nostoc, skytonema, Anabaena etc. have been found to be plentifully growing on Usar soils during the rains. He is of the opinion that the actual process of reclamation is a series of successive growth of the algal crop on such soils in a water-logged condition, consequently, he observed a decrease of pH, exchangeable sodium, sodium-calcium ratio and a corresponding increase in nitrogen, phosphorus, organic matter and water holding capacity of soil. One of the significant changes, however, was greater availability of soil phosphorus. Organic phosphorus of the nucleic acids, nucleotides etc. of the algal material is made available by dephosphorylation during the reclamation process for the subsequent use of crops. In the Banthra Farm near Lucknow, Kaul has tried reclamation of Usar soil by using blue green algae for neutralizing the alkalinity.

Chlorella forms a good energy material which can be added to the soil to raise its fertility. Little's[4] work in America on Chlorella pyrenoidosa has shown

it to be the most efficient with low intensity light of only 400 foot candles. His work also indicates that with improved techniques, an yield of 32½ tons of dry matter per acre would be obtained which is much higher than any recorded for cereals even under the most intensive condition of cultivation. It is also of interest to note that dry weight Chlorella possesses 50% proteins which figure, again, is four to five times the protein content of wheat grain.

With the above concept of the importance of Anabaena and Chlorella in increasing the fertility of soil, we have made an attempt to study the reclamation of alkaline soils with these algae alone and in combination with organic material like barley straw mixed with phosphate in the form of Tata basic slag.

Experimental Procedure

The following media recommended by De have been used for the growth of Anabaena naviculoides and Chlorella pyrenoidosa :

Medium for Anabaena		Medium for Chlorella	
KNO_3	0·2 gm.	NH_4NO_3	0·2 gm.
K_2HPO_4	0·2 gm.	K_2HPO_4	0·2 gm.
$MgSO_4.7H_2O$	0·2 gm.	$MgSO_4.7H_2O$	0·2 gm.
$CaCl_2$	0·1 gm.	$CaCl_2$	0·1 gm.
$FeCl_3$ (1%)	2 drops	$FeCl_3$ (1%)	2 drops
Distilled water	1000 c.c.	Distilled water	1000 c.c.

200 gm of well powdered soil obtained from Phulpur (Allahabad) was taken in enamelled dishes and mixed thoroughly with different organic matter and phosphate 50% distilled water was added and then the samples were inoculated with Anabaena naviculoides and Chlorella pyrenoidosa, already grown in De's media. In this way, two sets of experiments were performed under similar conditions. One set of experiments was exposed to artificial light from 100 watt electric bulb while the other set was covered with thick black cloth to cut off light. The temperature was recorded daily.

At the time of analysis, composite samples were taken and analysed for organic carbon, total nitrogen, exchangeable calcium, available P_2O_5, pH and electrical conductivity. Carbon was estimated by the method of Robinson, Mclean and Williams[5] and nitrogen by the salicylic acid reduction method[6]. Hissink's method[7] was used for the determination of exchangeable calcium and available phosphate was estimated by Dyer's method[8]. pH was determined by glass electrode Beckman pH meter[9] and conductivity was determined by a Leeds and Northrup Pt–Ir drum type bridge[10].

Results

Analysis of the alkali soil (oven dry) obtained from Phulpur (Allahabad)

Moisture	... 1·210%	Total nitrogen	... 0·0410%
Loss on ignition	... 2·820%	NH_3–N	... 0·0023%
HCl insoluble	... 84·190%	NO_3–N	... 0·0032%
Sesquioxide	... 7·050%	Available nitrogen	... 0·0055%
Fe_2O_3	... 4·1012%	pH	... 9·3
CaO	... 1·2502%	Conductivity	... 11·85 m.mhos/cm.
MgO	... 1·2400%	Total bacteria count ...	0·07 million/gm.
P_2O_5	... 0·1350%	Total Azotobacter count	... 0·04 million/gm.
K_2O	... 0·7920%		
Available P_2O_5	... 0·0280%	Total fungus count ...	0·012 million/gm.
Total carbon	... 0·2205%		

Analysis of Barley straw

					% *Chemical composition*
Loss on ignition	...	90·8592	MgO	...	0·1236
Ash	...	7·5670	K$_2$O	...	0·6215
Hcl insoluble	...	4·9852	P$_2$O$_5$	...	0·4832
Sesquioxide	...	1·5423	Total carbon	...	35 0520
Fe$_2$O$_3$	...	0·7321	Total nitrogen	...	0·5520
CaO	...	0·6532			

Analysis of Tata basic Slag

					% *Chemical composition*
Silica	...	22·560	Available P$_2$O$_5$	...	4·250
Sesquioxide	...	33·850	CaO	...	22·4560
Fe$_2$O$_3$	...	17·790	K$_2$O	...	8·8560
Al$_2$O$_3$	..	16·0250	MgO	...	4·0560
Total P$_2$O$_5$	...	7·570			

TABLE 1

200 *gm. Soil + Water* Av. Temp. 30°C

Period of exposure in days	Organic carbon (gm)	Total nitrogen (gm)	Efficiency	Exchange-able Ca (m.e. %)	Available P$_2$O$_5$ (gm)	Electrical conductivity in m.mhos/cm. (25°C)	pH
			Light				
0	0.4410	0·0820	...	4·80	0·0560	11·85	9·30
60	0·4225	0·0810	...	4·95	0·0562	11·82	9·25
120	0·4043	0·0802	...	5·08	0·0565	11·80	9·20
180	0·3865	0·0795	...	5·20	0·0567	11·78	9·15
240	0·3690	0·0788	. .	5·35	0·0570	11·75	9·15
			Dark				
0	0·4410	0·0820	...	4·80	0·0560	11·85	9·30
60	0·4310	0·0814	...	4·88	0·0561	11·83	9·30
120	0·4215	0·0809	..	4·95	0·0563	11·82	9·25
180	0·4123	0·0804	...	5·02	0·0565	11·81	9·20
240	0·4033	0·0800	...	5·08	0·0567	11·80	9·20

TABLE 2

200 *gm. Soil + 0·5% P$_2$O$_5$ as Tata basic slag*

Period of exposure in days	Organic carbon (gm)	Total nitrogen (gm)	Efficiency	Exchange-able Ca (m.e. %)	Available P$_2$O$_5$ (gm)	Electrical conductivity in m.mhos/cm. (25°C)	pH
			Light				
0	0·4410	0·0820	...	4·80	0·3367	11·85	9·30
60	0·4132	0·0814	.	5·05	0·3372	11·80	9·25
120	0·3960	0·0809	...	5·25	0·3375	11·78	9·20
180	0·3590	0·0804	...	5·40	0·3378	11·76	9·15
240	0·3323	0·0800	...	5·65	0·3380	11·74	9 15
			Dark				
0	0·4410	0·0820	...	4·80	0·3367	11·85	9·30
60	0·4268	0·0816	...	4·92	0·3370	11·82	9·30
120	0·4130	0·0813	...	5·02	0·3372	11·81	9·25
180	0·3994	0·0810	...	5·15	0·3375	11·80	9·20
240	0·3860	0·0807	..	5·25	0·3377	11·80	9·20

TABLE 3

200 gm. Soil + 1% C as Barley straw   Av. Temp. 30°C

Period of exposure in days	Organic carbon (gm)	Total nitrogen (gm)	Efficiency	Exchange able Ca (m.c.%)	Available P_2O_5 (gm)	Electrical conductivity in m. mhos/ cm. (25°C)	pH
			Light				
0	2·4410	0·1134	...	4·80	0·0560	11·85	9·30
60	1·7983	0·1267	20·8	6·90	0·0655	11·00	8·70
120	1·5462	0·1319	21·0	10·00	0·0788	10·50	8·55
180	1·3661	0·1356	20·6	12·25	0·0910	10·15	8·40
240	1·1876	0·1379	19·5	13·86	0·1102	9·90	8·30
			Dark				
0	2·4410	0·1134	...	4·80	0·0560	11·85	9·30
60	1·9256	0·1193	11·6	5·60	0·0607	11·56	8·90
120	1·7425	0·1213	11·3	7·25	0·0691	11·38	8·80
180	1·5597	0·1232	11·1	8·25	0·0772	11·20	8·70
240	1·3925	0·1246	10·6	9·55	0·0852	11·06	8·55

TABLE 4

200 gm. Soil + 1% C as Barley straw + 0·5% P_2O_5 Tata basic slag

Period of exposure in days	Organic carbon (gm)	Total nitrogen (gm)	Efficiency	Exchange able Ca (m.c.%)	Available P_2O_5 (gm)	Electrical conductivity in m. mhos/ cm. (25°C)	pH
			Light				
0	2·4410	0·1134	...	4·80	0·3367	11·85	9·30
60	1·5765	0·1434	34·8	8·35	0·3610	10·35	8·60
120	1·3142	0·1525	35·0	12·60	0·3904	9·04	7·80
180	1·1438	0·1582	34·5	16·05	0·4195	8·10	7·70
240	0·9738	0·1626	33·5	18·90	0·4477	7·30	7·60
			Dark				
0	2·4410	0·1134	...	4·80	0·3367	11·85	9·30
60	1·7620	0·1276	21·0	6·62	0·3465	10·72	8·80
120	1·5182	0·1331	21·3	8·60	0·3621	10·05	8·50
180	1·3325	0·1366	20·9	10·15	0·3774	9·45	8·20
240	1·1846	0·1386	20·0	11·35	0·3926	9·09	8·10

TABLE 5

200 gm. Soil + Anabaena naviculoides

Period of exposure in days	Organic carbon (gm)	Total nitrogen (gm)	Efficiency	Exchange able Ca (m.c.%)	Available P_2O_5 (gm)	Electrical conductivity in m. mhos/ cm. (25°C)	pH
			Light				
0	0·4410	0·0820	...	4·80	0·0560	11·85	9·30
60	0·4358	0·0815	...	5·15	0·0565	11·55	9·10
120	0·4173	0·0810	...	5·35	0·0569	11·30	8·90
180	0·3985	0·0803	...	5·75	0·0571	11·10	8·80
240	0·3785	0·0793	...	6·00	0·0573	10·95	8·70
			Dark				
0	0·4410	0·0820	...	4·80	0·0560	11·85	9·30
60	0·4312	0·0815	...	4·88	0·0561	11·83	9·30
120	0·4217	0·0810	...	4·95	0·0563	11·82	9·25
180	0·4124	0·0804	...	5·02	0·0565	11·81	9·20
240	0·4033	0·0800	. .	5·08	0·0567	11·80	9·20

TABLE 6

200 gm. Soil+Anabaena naviculoides+0·5% P₂O₅ as Tata Basic slag.   *Av. Temp. 30°C*

Period of exposure in days	Organic carbon (gm)	Total nitrogen (gm)	Efficiency	Exchange-able Ca (m.e.%)	Avail-able P₂O₅ (gm)	Electrical conductivity in m.mhos/ cm. (25°C)	pH
Light							
0	0·4410	0·0820	...	4·80	0·3367	11·85	9·30
60	0·4271	0·0819	...	5·35	0·3376	11·15	9·05
120	0·4001	0·0817	...	5·55	0·3380	10·75	8·85
180	0·3720	0·0812	...	6·05	0·3382	10·55	8·75
240	0·3449	0·0806	...	6·35	0·3383	10·45	8·65
Dark							
0	0·4410	0·0820	...	4·80	0·3367	11·85	9·30
60	0·4270	0·0818	...	4·92	0·3370	11·82	9·30
120	0·4132	0·0814	...	5·00	0·3372	11·81	9·25
180	0·3995	0·0811	..	5·08	0·3375	11·80	9·20
240	0·3860	0·0807	...	5·12	0·3377	11·80	9·20

TABLE 7

200 gm. Soil + 1% C as Barley straw + Anabaena naviculoides

	Organic carbon (gm)	Total nitrogen (gm)	Efficiency	Exchange-able Ca (m.e.%)	Avail-able P₂O₅ (gm)	Electrical conductivity	pH
Light							
0	2·4410	0·1134	...	4·80	0·0560	11·85	9·30
60	1·9807	0·1303	36·8	7·65	0·0660	10·60	8·55
120	1·7280	0·1391	36·0	10·80	0·0794	10·00	8·35
180	1·5450	0·1426	32·6	12·85	0·0945	9·20	8·15
240	1·3615	0·1431	27·5	14·35	0·1105	8·72	8·00
Dark							
0	2·4410	0·1134		4·80	0·0560	11·85	9·30
60	1·9258	0·1195	11·8	5·60	0·0607	11·56	8·90
120	1·7426	0·1214	11·9	7·25	0·0691	11·38	8·80
180	1·5597	0·1233	11·2	8·25	0·0772	11·20	8·70
240	1·2925	0·1246	10·6	9·55	0·0852	11·06	8·55

TABLE 8

200 gm. Soil + 1% C as Barley straw + 0·5% P₂O₅ as Tata basic slag +
Anabaena naviculoides

	Organic carbon (gm)	Total nitrogen (gm)	Efficiency	Exchange-able Ca (m.e.%)	Avail-able P₂O₅ (gm)	Electrical conductivity	pH
Light							
0	2·4410	0·1134		4·80	0·3367	11·85	9·30
60	1·7914	0·1488	54·4	9·75	0·3617	9·70	8·30
120	1·5286	0·1621	53·3	13·90	0·3912	8·35	7·55
180	1·2686	0·1711	49·2	17·05	0·4202	7·38	7·40
240	1·0852	0·1721	43·2	19·75	0·4482	6·65	7·25
Dark							
0	2·4410	0·1134		4·80	0·3367	11·85	9·30
60	1·7622	0·1277	21·1	6·62	0·3466	10·72	8·80
120	1·5183	0·1332	21·4	8·60	0·3622	10·05	8·50
180	1·3326	0·1367	21·0	10·15	0·3775	9·45	8·20
240	1·1846	0·1387	20·1	11·35	0·3926	9·09	8·10

TABLE 9

200 gm. Soil + Chlorella pyrenoidosa Av. Temp. 30°C

Period of exposure in days	Organic carbon (gm)	Total nitrogen (gm)	Efficiency	Exchangeable Ca (m.e.%)	Available P₂O₅ (gm)	Electrical conductivity m.mhos/cm. (25°C)	pH
			Light				
0	0·4410	0·0820		4·80	0·0560	11·85	9·30
60	0·4356	0·0811	...	5·00	0·0560	11·68	9·15
120	0·4170	0·0803	...	5·20	0·0568	11·42	8·95
180	0·3983	0·0795	..	5·55	0·0570	11·18	8·85
240	0·3784	0·0788	...	5·75	0·0572	11·02	8·75
			Dark				
0	0·4410	0·0820	...	4·80	0·0560	11·85	9·30
60	0·4311	0·0814	...	4·88	0·0561	11·83	9·30
120	0·4316	0·0809	...	4·95	0·0563	11·82	9·25
180	0·4124	0·0804	...	5·02	0·0565	11·81	9·20
240	0·4033	0·0800	...	5·08	0·0567	11·80	9·20

TABLE 10

200 gm. Soil + 0·5% P₂O₅ as Tata basic slag + Chlorella pyrenoidosa

Period of exposure in days	Organic carbon (gm)	Total nitrogen (gm)	Efficiency	Exchangeable Ca (m.e.%)	Available P₂O₅ (gm)	Electrical conductivity m.mhos/cm. (25°C)	pH
			Light				
0	0·4410	0·0820	...	4·80	0·3367	11·85	9·30
60	0·4268	0·0816	...	5·10	0·3375	11·26	9·10
120	0·3998	0·0811	...	5·30	0·3378	10·86	8·90
180	0·3718	0·0806	...	5·82	0·3381	10·68	8·80
240	0·3448	0·0801	...	6·15	0·3382	10·52	8·70
			Dark				
0	0·4410	0·0820	...	4·80	0·3367	11·85	9·30
60	0·4270	0·0816	...	4·92	0·3370	11·82	9·30
120	0·4132	0·0813	...	5·00	0·3372	11·81	9·25
180	0·3991	0·0810	...	5·08	0·3375	11·80	9·20
240	0·3861	0·0807	...	5·12	0·3377	11·80	9·20

TABLE 11

200 gm. Soil + 1% C as Barley straw + Chlorella pyrenoidosa

Period of exposure in days	Organic carbon (gm)	Total nitrogen (gm)	Efficiency	Exchangeable Ca (m.e.%)	Available P₂O₅ (gm)	Electrical conductivity m.mhos/cm. (25°C)	pH
			Light				
0	2·4410	0·1134	...	4·80	0·0560	11·85	9·30
60	1·9756	0·1271	29·4	7·55	0·0658	10·70	8·60
120	1·7231	0·1323	26·3	10·65	0·0791	10·12	8·40
180	1·5406	0·1359	24·9	12·62	0·0943	9·40	8·20
240	1·3576	0·1381	22·7	14·15	0·1103	8·90	8·05
			Dark				
0	2·4410	0·1134	...	4·80	0·0560	11·85	9·30
60	1·9258	0·1193	11·4	5·60	0·0607	11·56	8·90
120	1·72426	0·1213	11·1	7·25	0·0691	11·38	8·80
180	1·5598	0·1232	11·1	8·25	0·0772	11·20	8·70
240	1·3925	0·1246	10·6	9·55	0·0852	11·06	8·55

TABLE 12

200 gm. Soil + 1% C as Barley straw + 0·5% P_2O_5 as Tata basic slag + Chlorella pyrenoidosa   Av. Temp. 30°C

Period of exposure in days	Organic carbon (gm)	Total nitrogen (gm)	Efficiency	Exchange-able Ca (m.e. %)	Available P_2O_5 (gm)	Electrical conductivity in m.mhos/ cm. (25°C)	pH
Light							
0	2·4410	0·1134	...	4·80	0·3367	11·85	9·30
60	1·7862	0·1441	46·9	9·65	0·3615	9·92	8·40
120	1·5236	0·1532	43·3	13·75	0·3910	8·50	7·65
180	1·2638	0·1588	38·6	16·85	0·4200	7·55	7·50
240	1·0810	0·1631	36·5	19·55	0·4480	6·86	7·35
Dark							
0	2·4410	0·1134	...	4·80	0·3367	11·85	9·30
60	1·7622	0·1276	20·9	6·62	0·3466	10·72	8·80
120	1·5182	0·1331	21·3	8·60	0·3622	10·05	8·50
180	1·3326	0·1366	20·9	10·15	0·3775	9·45	8·20
240	1·1846	0·1386	20·1	11·35	0·3926	9·09	8·10

Discussion

From a perusal of the experimental results recorded in tables 5 to 12, it is clear that Anaba- na naviculoides and Chlorella pyrenoidosa did not grow well on alkali soil when they were used alone however, remarkable growth was obtained when they were used in conjunction with organic matter and phosphate. This can be explained on the basis that the soil reaction (pH 9·3) was not suitable for the growth of these algae and, moreover, the soil was deficient in the nutrients like available nitrogen, available phosphate, exchangeable calcium etc. necessary for their growth. Allison and co-worker[11] found that Nostoc muscorum grows best between pH 7·0 and 8·5 and Lund[4] reported that algae developed most freely on fertile soils well supplied with bases, available phosphates and nitrates and tend to be sparse in light, infertile and acid soils, Singh[3] carried out field experiments with blue green algae in alkali soils under water-logged condition and obtained good yield of paddy crop. Probably algae could grow well due to water-logging.

The experimental results recorded in tables 1 and 2, tables 5 and 6, tables 9 and 10 show that there is oxidation of carbon and loss of total nitrogen. With Anabaena naviculoides and Chlorella pyrenoidosa the oxidation of carbon is less due to the fact that some carbon is being added by the growth of these algae. The loss of nitrogen is minimised where Tata basic slag has been used as phosphatic material. This is because of the formation of stable phospho-proteins by the reaction of protein with phosphorus compounds. There is observed a lesser loss of nitrogen with Anabaena naviculoides as compared to Chlorella pyrenoidosa. This is due to the fixation of small amounts of nitrogen by Anabaena naviculoides. Practically, no growth of Anabaena and Chlorella was observed in the dark.

In tables 3 and 4, tables 7 and 8 and tables 11 and 12, results obtained by the addition of organic matter and phosphate inoculated with Anabaena naviculoides and Chlorella pyrenoidosa, have been recorded. It is noted from these tables that there is a marked saving of carbon in the case of Anabaena and Chlorella treated samples, although, the saving of carbon is slightly greater in the case of Anabaena. The efficiency of nitrogen fixation, i.e. the amount of nitrogen fixed in milligram per gram of carbon oxidised, is also greater in the case of samples treated with Anabaena naviculoides and Chlorella pyrenoidosa than the untreated ones. It is further noted that the efficiency of nitrogen fixation is greater in the

case of Anabaena than in the case of Chlorella because of the fact that Anabaena is capable of fixing atmospheric nitrogen.

From the experimental results recorded in tables 1 to 12, it is observed that the exchangeable calcium of the system increases with the oxidation of carbon. In the case of samples inoculated with Anabaena naviculoides and Chlorella pyrenoidosa, there is a greater increase of exchangeable calcium as compared to the samples where they have not been inoculated.

The experimental results recorded in tables 1 to 12 show that the available phosphate of the system increases with the oxidation of carbon. In the case of Anabaena and Chlorella treated samples, greater availability of phosphate is observed. Besides the increase in the availability due to the production of more carbonic acid and organic acids, the organic phosphorus of the nucleic acids, nucleotides etc. of the algal material is made available by dephosphorylation. Bower[12] showed that mono-nucleotides, nucleic acids and nucleo-proteins introduced into the soil by the incorporation of plant and animal residues or synthesised by soil microorganisms have been presumed to contain a major portion of soil organic phosphorus.

A perusal of the experimental results recorded in tables 1 to 12 clearly shows that the pH and electrical conductivity of the systems decrease with the oxidation of organic matter. It is observed that in the case of Anabaena and Chlorella treated samples, the decrease of pH and electrical conductivity is more pronounced as compared to the samples where Anabaena and Chlorella have not been applied. This is due to the greater amount of carbon added by the growth of these algae, and as a result more oxidation of carbon takes place producing greater amounts of carbonic and organic acids which are responsible for lowering down the pH of the systems. As a result of decrease in pH, more sodium salts like sulphates and chlorides are produced at the expense of sodium hydroxide present in alkali soils and thereby the electrical conductivity of the systems also decreases. This view can be supported by the work of Davies[13] and Glasstone[14]. This decrease is more pronounced in the case of Anabaena than in that of Chlorella, the reason being the greater growth of the former.

It is, therefore, concluded from my investigations that the efficiency of the process of reclamation of alkali soils with a mixture of organic matter and phosphates is increased to a greater extent when inoculated with Anabaena naviculoides and to a smaller extent when inoculated with Chlorella pyrenoidosa and that these algae are not markedly effective when applied alone to alkali soils.

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Nitrogen Loss from Soils, Part I. Retardation in Nitrogen Loss by Algae and Phosphates

By

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Abstract

Loss of humus and of nitrogen resulting by the addition of ammonium sulphate and ammonium nitrate to the soil was investigated. According to the observations the oxidation of organic carbon was enhanced by the addition of nitrogenous compounds. Moreover, much of the nitrogen added was lost to the air ; greater loss being suffered by ammonium sulphate. These transformations were pronounced in the sets receiving light.

The influence of algae, Anabaena naviculoides and Chlorella vulgaris, in presence and absence of phosphate (Tata basic slag) in retarding the loss of nitrogen was extensively studied. Loss of nitrogen was checked more by Chlorella than by Anabaena though the latter is a nitrogen fixer and the former is not. Loss of carbon also was checked by inoculating algae ; Chlorella being more effective than Anabaena. Available nitrogen in the algal sets was always less than that of the corresponding systems without algae.

The addition of phosphate also helped in retarding the nitrogen loss. Algae along with phosphate was most effective in checking the loss of nitrogen.

Introduction

A large amount of work is being carried on in understanding the role of nitrogenous fertilizers in land fertility and crop production. In addition to the deterioration of soil structure, soil tilth and permeability[1,2,3] by the use of nitrogenous fertilizers much of the added nitrogen is lost when conditions are favourable for oxidation.

Dhar and Coworkers[4,5], Bizell[6], Viswanath[7] and others[8-15] have reported loss of nitrogen from soils. Russell and Richards[16] and others[17-19] have observed considerable losses of nitrogen when nitrogenous substances were added to soils. Comparative study by Lohnis and Fred[20] of the three plant food materials from the field experiments revealed the following results :

Nitrogen%	Phosphorus%	Potassium%
7·8–46·1	10·1–75·6	22·4–85·1

Thus the loss of nitrogen posses a great threat to land fertility.

Although fixation of nitrogen in pure cultures [21-23] and in soils[24-26] by different species of blue-green algae have been reported but only a few have realised the importance of algae in retarding the loss of nitrogen. The first attempt was made by Gautier and Drouin[27]. They exposed artificial soil free from organic matter but containing ammoniacal nitrogen. In due course of time the soil was covered by algae. Loss in ammonia nitrogen and a gain in organic nitrogen and thus a corresponding decrease in the loss of total nitrogen was observed. Dhar and

Rishi[28] reported after 4 years of experimentation the retardation in nitrogen loss by algae.

To throw further light on the problem of nitrogen loss and its retardation, a number of experiments were conducted by the authors to investigate the influence of Anabaena naviculoides and Chlorella vulgaris, in presence and absence of phosphate, in checking the loss of nitrogen resulting by the addition of ammonium sulphate and ammonium nitrate to Allahabad soil.

Experimental

*Soil, rich in humus, was collected from the field in front of Sheila Dhar Institute for the experiments. 200 gms of the soil after passing through 60 mesh sieve was taken in 500 ml. conical flasks. 0·2% N as ammonium sulphate and ammonium nitrate was added to different flasks. 0·25% P_2O_5 was introduced and algae, Anabaena naviculoides and Chlorella vulgaris were inoculated wherever required. 40% moisture was maintained throughout the experimental period. Two similar sets were arranged ; one was exposed to light of a 500 watt electric bulb and the other was placed beside it covered by a thick black cloth. After 100, 200 and 300 days composite samples were taken out and analysed for total carbon, total nitrogen, ammoniacal and nitrate nitrogen and amino acids. Amino acids were detected by paper chromatography.

The following media were used for the growth of Anabaena naviculoides and Chlorella vulgaris.

Medium for Anabaena			Medium for Chlorella		
KNO_3	...	0·2 gm.	NH_4NO_3	...	0·2 gm.
K_2HPO_4	...	0·2 gm.	K_2HPO_4	...	0·2 gm.
$MgSO_4 7H_2O$	...	0·2 gm.	$MgSO_4 7H_2O$	...	0·2 gm.
$CaCl_2$	...	0·1 gm.	$CaCl_2$	...	0·1 gm.
$FeCl_3(1\%)$	..	3 drops	$FeCl_3(1\%)$	..	3 drops
Distilled water	...	1000 ml.	Distilled water	.	1000 ml.

Analysis of original soil and Tata basic slag.

% Analysis	Soil	Tata basic slag
Moisture	4·24	—
Loss on ignition	7·136	—
HCl insoluble	70·09	22·5421
Sesquioxide	10 873	33·7432
Fe_2O_3	4·327	17·7816
Al_2O_3	—	15·9622
CaO	5·081	22·4236
MgO	1·901	4·0426
P_2O_5	0·4683	7·9238
K_2O	1·5964	0·9158
Available P_2O_5	0·0431	4·0724
Total carbon	3·0088	—
Total nitrogen	0·2382	—
NH_3—N	0·0088	—
NO_3—N	0·0155	—
pH	7·65	—

*A sandy loam in which municipal rubbish has been incorporated for 10 years.

The amino acids identified have been abbreviated as follows :

Gly for glycine
Al for Alanine
Va for Valine
Se for Serine
Th for Threonine
Ly for Lysine

Ar for Arginine
Hi for Histidine
Glu for Glutamic acid
Asp for Aspartic acid
Pro for Proline

TABLE 1

200 gm. of soil + 0·2% N as ammonium sulphate   Av. Temp. 30°C

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Nitrogen loss %	NH₃—N gm.	NO₃—N gm.	Amino acids detected
Light						
0	6·0176	0·8764	—	0·4176	0·0310	Al., Ar., Glu.
100	5·4814	0·5849	33·3	0·1466	0·0701	Al., Ar., Glu.
200	5·1811	0·5133	41·4	0·0982	0·0835	Al., Glu., Va.
300	5·0162	0·4702	46·3	0·0645	0·0916	Glu., Va., Gly.
Dark						
0	6·0176	0·8764	—	0·4176	0·0310	Al., Ar., Glu.
100	5·6503	0·6471	26·2	0·2038	0·0588	Al., Ar., Glu.
200	5·4344	0·5972	31·9	0·1456	0·0697	Al., Ar., Glu.
300	5·3106	0·5606	36·0	0·1014	0·0755	Gly., Al., Glu.

TABLE 2

200 gms of soil + 0·2% N as ammonium nitrate

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Nitrogen loss %	NH₃—N gm.	NO₃—N gm.	Amino acids detected
Light						
0	6·0176	0·8764	—	0·2176	0·2310	Al., Ar., Glu.
100	5·4338	0·6736	23·1	0·1225	0·1447	Gly., Al., Ar., Glu.
200	5·0989	0·5907	32·6	0·0856	0·1155	Gly., Al., Va., Glu.
300	4·9244	0·5552	36·6	0·0729	0·1032	Gly., Al., Va., Glu.
Dark						
0	6·0176	0·8764	—	0·2176	0·2310	Al., Ar., Glu.
100	5·6229	0·7389	15·7	0·1534	0·1771	Al., Ar., Glu.
200	5·3852	0·6851	21·8	0·1295	0·1615	Gly., Al., Va., Glu.
300	5·2556	0·6533	25·5	0·1113	0·1494	Gly., Va., Glu.

TABLE 3

200 gms. of soil + 0·2% N as ammonium sulphate + 0·25% P₂O₅ as Tata basic slag

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Nitrogen loss %	NH₃—N gm.	NO₃—N gm.	Amino acids detected
Light						
0	6·0176	0·8764	—	0·4176	0·0310	Al., Ar., Glu.,
100	5·3838	0·6181	29·5	0·1598	0·0822	Al., Ar., Glu., Va.,
200	5·0482	0·5546	36·7	0·1165	0·0997	Al., Glu., Va., Hi.,
300	4·8610	0·5176	40·9	0·0859	0·1109	Al., Glu., Va., Gly.,
Dark						
0	6·0176	0·8764	—	0·4176	0·0310	Al., Ar., Glu.,
100	5·5722	0·6716	23·4	0·2151	0·0680	Al., Ar., Glu.,
200	5·3208	0·6273	28·4	0·1598	0·0821	Al., Ar., Glu., Gly.,
300	5·1762	0·5950	32·1	0·1188	0·0906	Al., Glu., Va., Gly.,

TABLE 4

200 *gms. of soil* + 0·2 % N *as ammonium nitrate* + 0·25% P_2O_5 *as Tata basic slag*

Av. Temp. 30°C

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Nitrogen loss %	NH_3—N gm.	NO_3—N gm.	Amino acids detected
			Light			
0	6·0176	0·8764	–	0·2176	0·2310	Al., Ar., Glu.,
100	5·3336	0·7116	18·8	0·1367	0·1580	Al., Ar., Glu., Va., Gly.
200	4·9595	0·6376	27·3	0·1050	0·1327	Al., Glu., Va., Gly., Hi.
300	4·7642	0·6097	30·4	0·0952	0·1233	Al., Glu., Va., Gly.,
			Dark			
0	6·0176	0·8764	–	0·2176	0·2310	Al., Ar., Glu.
100	5·5143	0·7665	12·5	0·1655	0·1873	Al., Ar., Glu.,
200	5·2680	0·7187	17·8	0·1447	0·1748	Al., Ar., Glu., Gly.,
300	5·1174	0·6915	21·1	0·1296	0·1658	Glu., Gly., Va.,

TABLE 5

200 *gms. of soil* + 0·2% N *as ammonium sulphate* + *Chlorella*

Light

0	6·0176	0·8764	–	0·4176	0·0310	Al., Ar., Glu.,
100	5·5911	0·6216	29·1	0·1399	0·0663	Al., Glu. Va., Asp.,
200	5·3243	0·5561	36·5	0·0893	0·0782	Al., Glu., Va., Asp., Pro.
300	5·1505	0·5114	41·6	0·0569	0·0870	Al., Glu., Va., Asp., Pro. Se., Th.,

TABLE 6

200 *gms. of soil* + 0·2% N *as ammonium nitrate* + *Chlorella*

Light

0	6·0176	0·8764	–	0·2176	0·2310	Al., Ar., Glu.,
100	5·5556	0·7154	18·4	0·1146	0·1405	Al., Ar., Glu., Va. Asp.
200	5·2519	0·6386	27·1	0·0753	0·1097	Al., Glu., Va., Asp., Pro.,
300	5·0669	0·6015	31·4	0·0641	0·0982	Al., Glu., Va., Asp., Pro., Th., Se.,

TABLE 7

200 *gms. of soil* + 0·2% N *as ammonium sulphate* + *Anabaena*

Light

0	6·0176	0·8764	–	0·4176	0·0310	Al., Ar., Glu.,
100	5·5648	0·6147	29·9	0·1439	0·0655	Al., Glu., Va., Asp.,
200	5·2903	0·5482	37·4	0·0942	0·0770	Al., Glu., Va., Asp., Se.
300	5·1204	0·5034	42·6	0·0612	0·0862	Al., Glu., Va., Asp., Se. Th.

TABLE 8

200 gms. of soil + 0·2% N as ammonium nitrate + Anabaena Av. Temp. 30°C

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Nitroten loss %	NH_3—N gm.	NO_3—N gm.	Amino acids detected
			Light			
0	6·0176	0·8764	–	0·2176	0·2310	Al., Ar., Glu.,
100	5·5273	0·7075	19·3	0·1195	0·1397	Al., Glu., Va. Asp., Se.
200	5·2173	0·6297	28·1	0·0813	0·1085	Al., Glu., Va., Asp., Se. Th.
300	5·0355	0·5925	32·4	0·0693	0·0974	Al., Glu., Va., Asp., Se. Th.

TABLE 9

200 gms. of soil + 0·2% N as ammonium sulphate + 0·25% P_2O_5 as Tata basic slag + Chlorella

			Light			
0	6·0176	0·8764	–	0·4176	0·0310	Al., Ar., Glu.,
100	5·5076	0·6587	24·8	0·1523	0·0780	Al., Ar., Glu., Va., Pro.
200	5·2095	0·6031	31·2	0·1068	0·0941	Al., Ar., Glu., Va., Pro. Se.
300	5·0135	0·5644	35·6	0·0776	0·1061	Al., Ar., Glu., Va., Pro., Se., Th., Hi.

TABLE 10

200 gms. of soil + 0·2% N as ammonium nitrate + 0·25% P_2O_5 as Tata basic slag + Chlorella

			Light			
0	6·0176	0·8764	–	0·2176	0·2310	Al., Ar., Glu.,
100	5·4695	0·7573	13·6	0·1280	0·1533	Al., Ar., Glu., Va., Asp., Pro.
200	5·1328	0·6911	21·1	0·0939	0·1264	Al., Ar., Va., Asp., Pro., Se., Th.
300	4·9249	0·6615	24·5	0·0857	0·1179	Al., Ar., Va., Asp., Pro., Se., Th., Hi.,

TABLE 11

200 gms. of soil + 0·2% N as ammonium sulphate + 0·25% P_2O_5 as Tata basic slag + Anabaena

			Light			
0	6·0176	0·8764	–	0·4176	0·0310	Al., Ar. Glu.
100	5·4811	0·6501	25·8	0·1568	0·0772	Al., Ar., Glu., Va., Se.
200	5·1725	0·5947	32·1	0·1113	0·0928	Al., Ar., Glu., Va., Se., Asp., Hi.
300	4·9824	0·5559	36·6	0·0817	0·1049	Al., Glu., Va., Se., Asp., Hi., Th.

TABLE 12

200 gms. of soil + 0.2% N as ammonium nitrate + 0.25% P$_2$O$_5$ as Tata basic slag + Anabaena   Av. Temp. 30°C

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	Nitrogen loss %	NH$_3$—N gm.	NO$_3$—N gm.	Amino acids detected
			Light			
0	6·0176	0·8764	—	0·2176	0·2310	Al., Ar., Glu.
100	5·4409	0·7485	14·6	0 1334	0·1526	Al., Glu., Va.. Se., Asp.
200	5·0950	0·6827	22·1	0·1002	0·1253	Al., Glu., Va., Se., Asp. Hi., Ly.
300	4·8924	0·6531	25·5	0·0913	0·1170	Al., Glu., Va., Se.. Asp., Hi., Ly., Th.

TABLE 13

Percentage loss of nitrogen after 300 days

Treatement		Alone	With T.B.S.	With Chlorella	With Anabaena	With Chlorella + T.B.S.	With Anabaena + T.B.S.
Ammonium Sulphate	Light	46·3	40·9	41·6	42·6	35·6	36·6
	Dark	36·0	32·1	—	—	—	—
Ammonium Nitrate	Light	36·6	30·4	31·4	32·4	24·5	25·5
	Dark	25·5	21·1	—	—	—	—

Discussion

The results recorded in Table 13 indicate greater loss of nitrogen from the system containing ammonium sulphate than that of the system containing ammonium nitrate. Moreover, greater loss is suffered by the systems exposed to light than those covered by black cloth. Correspondingly there is a decrease in the total available nitrogen more so in the sets exposed to light (Tables 1 and 2).

Hence, it is deduced from these results that much of the added nitrogen is lost to the air and this loss is enhanced by light radiations. Dhar and Pant[29] have reported losses of nitrogen in soils and oxide surfaces even in the complete absence of microorganisms.

The most plausible explanation for this loss of nitrogen is that under aerobic conditions the proteins present in the soil and other nitrogenous substances undergo the following changes :

$$\text{Proteins} \longrightarrow \text{amino acids} \xrightarrow{\text{(+O}_2\text{)}} \text{NH}_4 \text{ compounds}$$

$$\text{NO}_3 \xleftarrow{\text{(+O}_2\text{)}} \text{NO}_2 \xleftarrow{\text{(+O}_2\text{)}} $$
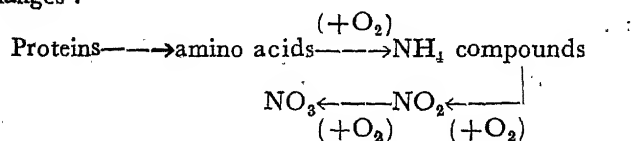
These changes being oxidation reactions are accelerated by light absorption and temperature increase. During these reactions the possibility of the formation of

an unstable and explosive substance, ammonium nitrate, is always there. It is well known that ammonium nitrate suffers oxidation and decomposition aided by light as follows :

$$2NH_4NO_2 + O_2 = 2NH_4NO_3$$
$$NH_4NO_2 = N_2 + 2H_2O + 718 \text{ K. cals.}$$
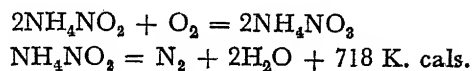
The second reaction is more prominent than the first and hence, there is considerable loss of nitrogen.

From the summarised results recorded in Table 13 it is quite evident that phosphate as Tata basic slag retards nitrogen loss considerably, the retardation being more pronounced in light. Moreover, there is an increase in the total available nitrogen and the free amino acids (Vide Table 3 and 4).

The retardation in nitrogen loss by phosphates can be explained from the following considerations :

Firstly, phosphates form complex phosphoproteins which are more stable than proteins and amino acids. Secondly, calcium present in the slag can react with nitrite ions forming calcium nitrite which is more stable than ammonium nitrite.

In all the systems inoculated with algae, changes are observed only in the systems exposed to light—showing, thereby, that algae do not grow in the dark.

From a careful perusal of tables 5 to 12 it is observed that there is some saving of carbon in all the systems inoculated with algae and exposed to light — greater saving of carbon is recorded in the systems having Chlorella than those having Anabaena. This observation can be attributed to the faster growth rate of Chlorella than Anabaena[25]. Moreover, the saving of carbon is more pronounced in the phosphated systems than in the unphosphated sets showing, thereby, that phosphates enhance the growth of algae.

A further perusal of the summarised results recorded in Table 13 indicates that algae also retard the loss of nitrogen and the loss is checked more by Chlorella than by Anabaena though Anabaena is a nitrogen fixer. The retardation is more pronounced when algae and phosphates are introduced together. The total available nitrogen is always less in the algal sets than those of the sets without algae ; the number of amino acids being more in the algal sets.

The retardation in nitrogen loss by algae seems to be due to the fact that algae, for their own growth, take available nitrogen from the system and thus a part of the available nitrogen is converted into organic nitrogen which is comparatively stable. At the same time carbohydrates and proteins synthesised by algae exert a negative catalytic effect on the nitrogen changes resulting in the formation of ammonium nitrate.

Hence, from these investigations we conclude that phosphates as well as algae retard the loss of nitrogen resulting by the addition of nitrogenous fertilisers to soils. The maximum retardation of nitrogen loss is observed when both, algae (Chlorella or Anabaena) and phosphate, are incorporated together into soils.

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Precipitation and Solubility of Chromium Phosphate
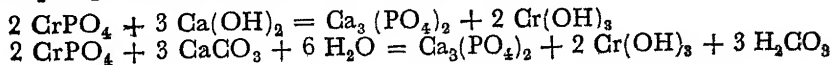
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Chromium phosphate was prepared by allowing a mixture of chromium nitrate and disodium hydrogen phosphate to react at room temperature with agitation for 5–6 hours. The precipitate so formed was filtered off, washed rapidly with water and then with ethyl alcohol. It was then dried in an oven at 80°C, analysed for its constituents and found to have the composition, $1 \cdot 05$ Cr_2O_3. P_2O_5. $12 \cdot 08$ H_2O. This shows that the precipitation of the phosphate from chromium nitrate solution and disodium hydrogen phosphate proceeds by the following equation :

$$Cr(NO_3)_3 + Na_2HPO_4 = CrPO_4 + 2\,NaNO_3 + HNO_3$$
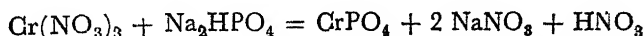
The precipitated phosphate has been observed to undergo hydrolysis in water with the liberation of small amounts of P_2O_5 and Cr_2O_3. The amounts of P_2O_5 and Cr_2O_3 passing into the solution at 30°C are $0 \cdot 3014$ and $0 \cdot 2533$ millimoles per litre respectively. It has also been observed that the rate of hydrolysis increases with temperature and greater amounts of P_2O_5 and Cr_2O_3 pass into the solution.

Calcium oxide and calcium carbonate have been found to facilitate the hydrolysis of chromium phosphate, due to its decomposition into more soluble calcium phosphates according to the following equations :

$$2\,CrPO_4 + 3\,Ca(OH)_2 = Ca_3\,(PO_4)_2 + 2\,Cr(OH)_3$$
$$2\,CrPO_4 + 3\,CaCO_3 + 6\,H_2O = Ca_3(PO_4)_2 + 2\,Cr(OH)_3 + 3\,H_2CO_3$$

Weak organic acids *viz*., acetic, formic, tartaric and citric have been found to increase the solubility of precipitated chromium phosphate to different extents. On the basis of their dissolving action on the phosphate, these acids can be arranged in the following order :

Citric > Tartaric > Formic > Acetic

It appears that the structural characteristics of the organic anion and H^+ ion concentration play an important role in increasing the solubility of the phosphate. Carbonic acid, however, has been found to have a depressing effect on the solubility of the phosphate. This is due to the fact that basic character of chromium hydroxide is not high and, therefore, formation of carbonate and bicarbonate takes place with difficulty and, therefore, a decrease in the solublity.

Thus it is evident from the observations recorded above that various organic acids which are formed during the slow oxidation of organic matter as intermediate products are more effective than the final product carbonic acid in dissolving the phosphate and thus making them available for crops in soils.

Alkalies have been observed to have a decomposing effect on the phosphate. Maximum decomposition has been observed with sodium hydroxide, followed by sodium carbonate and sodium bicarbonate in which it is least. The action of

alkalies on the phosphate has been explained on the solubility product consi-
derations.

The solubility of chromium phosphate has been found to increase markedly in presence of decomposing organic matter like glucose, wheat straw and finely divided bituminous coal. Of these glucose has been observed to cause maximum increase in the solubility of the phosphate. This is due to the fact that glucose being a soluble carbohydrate is readily oxidised whereas wheat straw, a chiefly cellulosic material and bituminous coal, a petrified organic matter are not easily oxidised. The increase in the solubility of the phosphate in presence of decom-posing organic substances has been attributed to the dissolving action of various organic acids which are produced as intermediate products during its decom-position and oxidation.

Details will be published elsewhere.

Nitrogen Loss from Soils, Part II. Retardation in Nitrogen Loss by Organic matter and Phosphate

By

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Abstract

The influence of organic matter (wheat straw) in presence and absence of phosphate (Tata basic slag) on checking the loss of nitrogen resulting by the addition of ammonium sulphate and ammonium nitrate to the soil was studied.

The loss of nitrogen was appreciably checked by the addition of organic matter and the retarding influence was much pronounced when phosphate was incorporated along with organic matter. There was an increase in the available nitrogen in the systems having organic matter and phosphate. From these investigations it has been concluded that the addition of organic matter and phosphate is essential for maintaining the nitrogen and humus of soils.

Introduction

The value of organic matter in land fertility has been realized from ancient times. Considering its importance Joh B. Abbot[1] of Vermont, U. S. A. states : "If all accumulated soil wisdom of a hundred generations of master farmers were boiled down to just three sentences, one of these sentences certainly would be : provide for regular and frequent replenishment of the supply of organic matter in the soil".

Rahn[2] found that phosphatic manures were available only when used in conjunction with organic matter. Hester and Shelton[3], Metzger[1] and Scarseth[5] and others[6-8] reported that organic matter has a beneficial effect in keeping the phosphate available for plant use.

The advantages of incorporating organic matter along with phosphatic fertilizers into the soil are widely realized. This information has been derived from the plant uptake and response data. Dhar[9], Levin[10], Sandhoff[11] and others[12-21] have reported that by the addition of organic matter and phosphate to soils, much better results are obtained than with either of them when used alone. An increase in the fertilizing efficiency was observed when manure was reinforced with 25–40 lbs. of super phosphate or 40–80 lbs. of rock phosphates per ton[22].

In the U. S. A.[23] the following results were obatined showing marked nitrogen fixation and increased corn yield by a mixture of phosphate and manure :

Average of three field treatments	Nitrogen in soil per acre in lbs.	Corn yield in bushels per acre.
No manure	1600	17
Manure	1760	36
Manure + phosphate	1990	51

Recently basic slag has found a world wide application as the phosphating fertilizer in soils. Hamawi and Hashish[24] observed an increased efficiency of basic slag in physiologically acid conditions. Ling and Muir[25] and Gasiorowski[26] and others[27-30] have reported beneficial effect of basic slag on crop production. Dhar[31] has obtained greater yields of paddy and wheat when organic matter was ploughed along with basic slag.

Generally better yield of crops has been observed with a mixture of mineral nitrogen and organic matter than with mineral nitrogen alone[32-34]. The Norfolk rotation experiments by Rayns and Culpin[35] show better yields of crops with a mixture of ammonium sulphate and dung or ammonium sulphate and straw than with mineral nitrogen when used alone. Johnson[36] found that the average yield of potatoes was 155 bushels when one ton of a 6–4–8 fertilizer was added but when a green manure crop was turned under previous to the additions of the fertilizer, the average yield was raised to 232 bushels.

Keeping all these researches in view we carried out the present experiments to study retardation in nitrogen loss by organic matter (wheat straw) and phosphate (Tata basic slag).

Experimental

0·2% N as ammonium sulphate and ammonium nitrate was added to different flasks containing 200 gms of soil in each flask. Wheat straw (1% C) and Tata basic slag (0·25% P_2O_5) was introduced into the flasks. 40% moisture was maintained throughout the experimental period. Two similar sets were arranged, one was exposed to the light of a 500 watt electric bulb and the other was covered by thick black cloth. Composite samples were analysed after 100, 200 and 300 days for total carbon, total nitrogen, ammoniacal and nitrate nitrogen and amino acids.

Analysis of original soil and wheat straw

% Analysis	Soil	Wheat straw
Moisture	4·24	–
Loss on ignition	7·136	91·0165
HCl insoluble	70·09	6·1286
Sesquioxide	10·873	1·4296
Fe_2O_3	4·327	0·6682
Al_2O_3	–	–
CaO	5·081	0·6554
MgO	1·901	0·1376
P_2O_5	0·4683	0·4903
K_2O	1·5964	0·7788
Available P_2O_5	0·0431	–
Total carbon	3·0088	38·1643
Total nitrogen	0·2382	0·5902
NH_3—N	0·0088	–
NO_3—N	0·0155	–
pH	7·65	–

The amino acids identified have been abbreviated as follows :

Gly for glycine   Ar for Arginine

Al for Alanine   Hi for Histidine

Va for Valine   Glu for Glutamic acid

Se for Serine   Asp for Aspartic acid

Th for Threonine   Pro for Proline

Ly for Lysine   Leu for Leucine

TABLE 1

200 gms. Soil + 0·2% N as ammonium Sulphate + 1% carbon as wheat straw

Av. Temp. 30°C

Period of exposure in days	Total carbon (gm)	Total nitrogen (gm)	Nitrogen loss %	NH_3—N (gm)	NO_3—N (gm)	Amino acids detected
			Light			
0	8·0176	0·9073	—	0·4176	0·0310	Al, Ar, Glu.
100	6·6669	0·6576	27·5	0·1798	0·0892	Al, Ar, Glu, Va, Leu.
200	5·8349	0·6058	33·2	0·1435	0·1097	Al, Ar, Glu, Va, Leu., Gly.
300	5·3673	0·5797	36·1	0·1169	0·1229	Al, Glu, Va, Leu, Gly, Asp.
			Dark			
0	8·0176	0·9073	—	0·4176	0·0310	Al, Ar, Glu.
100	7·0727	0·7028	22·5	0·2320	0·0739	Al, Ar, Glu, Va.
200	6·4606	0·6668	26·5	0·1818	0·0899	Al, Ar, Glu, Va, Gly.
300	6·0524	0·6400	29·5	0·1444	0·0997	Al, Glu, Va, Gly., Asp.

TABLE 2

200 gms. Soils + 0·2% N as ammonium nitrate + 1% carbon as wheat straw

Period of exposure in days	Total carbon (gm)	Total nitrogen (gm)	Nitrogen loss %	NH_3—N (gm)	NO_3—N (gm)	Amino acids detected
			Light			
0	8·0176	0·9073	—	0·2176	0·2310	Al, Ar, Glu.
100	6·5992	0·7491	17·4	0·1576	0·1689	Al, Ar, Glu, Va, Gly,
200	5·7608	0·6874	24·2	0·1329	0·1486	Al, Glu, Va, Gly, Leu.
300	5·2056	0·6700	26·2	0·1273	0·1424	Al, Va, Gly, Glu, Leu, Asp.
			Dark			
0	8·0176	0·9073	—	0·2176	0·2310	Al, Ar, Glu.
100	7·0339	0·7963	12·2	0·1835	0·1973	Al, Ar, Glu, Gly,
200	6·4136	0·7574	16·5	0·1675	0·1885	Al, Glu, Gly, Va.
300	5·9734	0·7358	18·9	0·1566	0·1815	Al, Glu, Gly, Va, Asp.

TABLE 3

200 gms. soil + 0·2% N as ammonium sulphate + 1% carbon as wheat straw + 0·25% P_2O_5 as Tata basic slag   *Av. Temp. 30°C*

Period of exposure in days	Total carbon (gm)	Total nitrogen (gm)	Nitrogen loss %	NH_3—N (gm)	NO_3—N (gm)	Amino acids detected
			Light			
0	8·0176	0·9073	—	0·4176	0·0310	Al, Ar, Glu.
100	6·5084	0·6967	23·2	0·1949	0·1038	Al, Ar, Glu, Va, Leu, Gly.
200	5·6266.	0·6362	27·7	0·1636	0·1278	Al, Glu, Va, Leu, Gly, Asp.
300	5·1365	0·6382	29·7	0·1401	0·1440	Al, Glu, Va, Leu, Gly, Asp, Hi.
			Dark			
0	8·0176	0·9073	—	0·4176	0·0310	Al, Ar, Glu.
100	6·9402	0·7323	19·3	0·2449	0·0849	Al, Ar, Glu, Gly, Va.
200	6·3025	0·7047	22·3	0·1979	0·1038	Al, Ar, Glu, Gly, Va, Leu
300	5·8668	0·6830	24·7	0·1636	0·1167	Al, Glu, Gly, Va, Leu, Asp.

TABLE 4

200 gms. Soil + 0·2% N as ammonium nitrate + 1% carbon as wheat straw + 0·25% P_2O_5 as Tata basic slag

Period of exposure in days	Total carbon (gm)	Total nitrogen (gm)	Nitrogen loss %	NH_3—N (gm)	NO_3—N (gm)	Amino acids detected
			Light			
0	8·0176	0·9073	—	0·2176	0·2310	Al, Ar, Glu.
100	6·4383	0·7933	12·6	0·1740	0·1849	Al, Ar, Glu, Va, Leu, Gly.
200	5·5484	0·7436	18·0	0·1541	0·1688	Al, Glu, Va, Leu, Gly, Asp, Hi.
300	4·9705	0·7367	18·8	0·1512	0·1658	Al, Glu, Va, Leu, Gly, Asp, Hi.
			Dark			
0	8·0176	0·9073	—	0·2176	0·2310	Al, Ar, Glu.
100	6·9049	0·8291	8·6	0·1976	0·2102	Al, Ar, Glu, Gly, Va.
200	6·2513	0·7991	11·9	0·1846	0·2047	Al, Ar, Glu, Gly, Va, Leu.
300	5·7832	0·7829	13·7	0·1765	0·2007	Al, Glu, Gly, Va, Leu, Asp

TABLE 5

Percentage loss of nitrogen after 300 days

Treatment		Alone	With wheat straw	With wheat straw and Tata basic slag
Ammonium sulphate	Light	46·3	36·1	29·7
	Dark	36·0	29·5	24·7
Ammonium nitrate	Light	36·6	26·2	18·8
	Dark	25·5	18·9	13·7

Discussion

The condensed results recorded in Table 5 indicate clearly that wheat straw appreciably retards the loss of nitrogen more so in the systems exposed to light. Comparative results of retardation by algae (Part 1) and organic matter show that wheat straw is more effective than algae in checking the loss of nitrogen. The retardation in nitrogen loss being more pronounced when phosphate as Tata basic slag is incorporated along with wheat straw.

The retardation by wheat straw is explained from the viewpoint that carbonaceous matter acts as negative catalyst and retards the process of nitrification, an oxidation reaction, in which there is always the possibility of the formation of the unstable and explosive substance, ammonium nitrite, which breaks to give nitrogen gas as explained earlier. It is well known that carbohydarates act as protein sparers in the animal body. Similarly the soil carbonaceous substances like cellulose, lignin etc. retard the oxidation of proteins, amino acids and ammonium salts by air and thus act as protectors of soil nitrogen. Rishi[37] has observed that the oxidation of proteins and amino acids like gelatine, glycine, hippuric acid and creatine in soils is markedly retarded when wheat straw is incorporated into the soils. Dhar[38] has shown that carbohydrates and fats act as negative catalysts and retard the oxidation of amino acid and proteins.

This conclusion is further supported by the observations that the number of amino acids and the total available nitrogen is always more in the systems containing wheat straw and slag than those of the systems without these substances.

Hirschler[39] pointed out that the decomposition of protein by micro-organisms is modified by the presence of carbohydrates. According to him bacteria do not decompose large amounts of protein in presence of available carbohydrates. This factor may also contribute to the retardation of nitrogen loss by carbonaceous matter.

Moreover, the organic matter (in the form of wheat straw) when added to soil surface undergoes slow oxidation aided by air and light and liberates energy in this process, which is utilized in fixing atmospheric nitrogen. Thus, a part of the nitrogen lost is compensated by the fixation of atmospheric nitrogen.

The pronounced retardation in presence of Tata basic slag is due to the fact that phosphates form phosphoproteins with the proteins and nitrogenous compounds in the soil, which are more resistant to oxidation than proteins, amino acids and ammonium salts. Moreover, phosphates markedly increase nitrogen fixation in presence of organic matter.

Thus, it is concluded from the foregoing observations and discussion that the addition of nitrogenous fertilizers should always be supplemented by a mixture of organic matter and phosphate if the nitrogen and humus status of soils and, thereby, the fertility has to be maintained or increased.

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Enhanced Oxidation of Carbohydrates in the nitrification of inorganic nitrogenous fertilisers

By

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For a longtime the organic school of crop production *i.e.,* those who decay the use of artificial fertilisers alone have stated that humus loss or carbon oxidation by air is accentuated by adding nitrogenous fertilisers. Fox has shown that ammonium sulphate may bring about the breakdown of soil structure. Ruschmann holds the view that mineral nitrogenous fertilisers accelerate the breaking down of soil humus. Dhar and Coworkers have carried out a large number of experiments regarding the influence of different nitrogenous compounds on the oxidation of soil humus and have shown that in presence of nitrogenous fertilisers the humus carbon is oxidised by air at a greater speed than in their absence. In view of the above considerations further experiments were carried out to observe the effect of inorganic nitrogenous fertilisers on the oxidation of carbohydrates.

Experimental Procedure

2·5 gms of washed oven dried and sieved titania were weighed into a large number of conical flasks. To each of these flasks were added 400 c.c. of a solution containing 2% carbon as glucose. All these flasks were plugged with cotten wool and exposed to light from a 100 watt electric bulb for 6–8 hours daily. An identical set of flasks was next prepared, covered with a thick black cloth to cut off all light and placed alongside the exposed flasks.

The above procedure was repeated using solutions containing 6% carbon as glucose, 0·05% or 0·1% nitrogen as ammonium sulphate and 2% or 6% carbon as glucose, 0·05% or 0·1% nitrogen as ammonium nitrate plus 2% or 6% carbon as glucose 0·05% or 0·1% nitrogen as calcium nitrate plus 2% or 6% carbon as glucose and suspensions containing 2% or 6% carbon as starch, 2% or 6% carbon as starch plus 0·05% or 0·1% nitrogen as ammonium sulphate, 2% or 6% carbon as starch plus 0·05% or 0·1% nitrogen as ammonium nitrate and 2% or 6% carbon as starch plus 0·05% or 0·1% nitrogen as calcium nitrate. In every case 2·5 gms of titania were used as surface and 400 c.c. of the solution or suspension introduced into each flask.

All the flasks were shaken for a few minutes daily and after definite intervals of time the contents of one flask from each set was transferred to a pestle, well ground and transferred to a 500 c.c. volumetric flask the volume made up and aliquot portions analysed for total carbon according to the methods of Robinson and Mclean and Williams.

Our experimental results indicate that the oxidation of carbon is enhanced when inorganic nitrogenous fertilisers are added to aqueous solutions or suspensions of glucose or starch in presence of titania as a surface both in exposed and covered systems though always greater in the former than in the latter.

Our results also show that the oxidation of carbon with 2% and 6% carbon as glucose or starch is in the following descending order.

Calcium nitrate > ammonium nitrate > ammonium sulphate.

System	% Carbon oxidation after 180 days	
	Light	*Dark*
2% carbon as glucose	31·10	22·05
2% carbon as glucose + 0·05% N as ammonium sulphate	34·20	22·16
2% carbon as glucose + 1% N as ammonium sulphate	36·90	23·85
2% carbon as glucose + 0·05% N as ammonium nitrate	36·90	24·91
2% carbon as glucose + 0·1% N as ammonium nitrate	39·30	26·30
2% carbon as glucose + 0·5% N as calcium nitrate	40·60	27·46
2% carbon as glucose + 0·1% N as calcium nitrate	50·40	32·65
2% carbon as starch	26·30	17·05
2% carbon as starch + 0·05% N as ammonium sulphate	28·20	19·05
2% carbon as starch + 0·1% N as ammonium sulphate	29·50	19·51
2% carbon as starch + 0·05% N as ammonium nitrate	31·50	21·05
2% carbon as starch + 0·1% N as ammonium nitrate	36·31	23·90
2% carbon as starch + 0·05% N as calcium nitrate	34·25	23·00
2% carbon as starch + 0·1% N as calcium nitrate	41·90	27·00
6% carbon as glucose	18·87	12·66
6% carbon as glucose + 0·5% N as ammonium sulphate	20·06	13·22
6% carbon as glucose + 0·1% N as ammonium sulphate	21·06	13·35
6% carbon as glucose + 0·05 N as ammonium nitrate	22·30	14·36
6% carbon as glucose + 0·1% N as ammonium nitrate	25·46	16·50
6% carbon as glucose + 0·05% N as calcium nitrate	24·80	16·33
6% carbon as glucose + 0·1% N as calcium nitrate	30·50	19·93
6% carbon as starch	13·61	8·77
6% carbon as starch + 0·05% N as ammonium sulphate	14·43	9·65
6% carbon as starch + 0·1% N as ammonium sulphate	15·26	10·05
6% carbon as starch + 0·05% N as ammonium nitrate	16·93	11·05
6% carbon as starch + 0·1% N as ammonium nitrate	20·16	13·27
6% carbon as starch + 0·05% N as calcium nitrate	18·91	12·38
6% carbon as starch + 0·1% N as calcium nitrate	23·91	15·38

As the initial concentration of the various nitrogenous compounds used was raised from 0·05% nitrogen to 0·1% nitrogen there was observed an increase in the rate as well as the amount of carbon oxidised in the various systems. Moreover this increase was always observed to be greater in light than in dark.

Allison and Murphy found that when finely ground woods and barks from a tree species were incubated with a sandy loam, leached of nitrogen and mixed with known amounts of urea or ammonium nitrate an average of 30·3% of the wood carbon was released as carbondioxide in the absence of nitrogen in the first 60 days while 45·1% was released in its presence. The corresponding values for bark were 22·4 and 24·5% respectively.

Similarly Lucken, Hutchean and Paul found that addition of ammonium nitrate accelerated the initial decomposition of wheat straw and lucerne in clay loams of 6% and 1·64% organic carbon incubated with various crop residues.

It seems that in presence of these nitrogenous fertilisers the main end product of nitrification is nitrate which being a marked oxidising agent can directly react with the carbonaceous compounds and oxidise them. This point is further supported by our experimental results which show that calcium nitrate and ammonium nitrate enhance the oxidation of glucose and starch to a greater extent than does ammonium sulphate.

Fixation of Nitrogen by Algae in Presence and Absence of Wheat Straw and Basic Slag

By

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Abstract

Nitrogen fixation by blue-green algae, Anabaena naviculoides and Tolypothrix tenuis, in Allahabad loam was studied. Observations show Tolypothrix as a better nitrogen fixer than Anabaena.

Compared to the nitrogen fixed by organic matter and phosphate the amounts fixed by algae are small.

Experimental results indicate that growth of algae and, thereby, the efficiency of nitrogen fixation by algae is enhanced in presence of wheat straw and Tata basic slag.

Introduction

Some blue-green algae of the family Nostococaceae have been observed to fix atmospheric nitrogen. The first evidence in this regard was provided by Franck[1] in 1889. Fixation in pure cultures was later confirmed by Drewes[2], Fogg[3] and De[4]. Allison and Morris[5] and others[6,7] observed nitrogen fixation with other species. 10–20 mg of nitrogen per 100 ml were fixed in 50–60 days with pure cultures of Nostoc[8].

Jensen[9] observed a gain of 2·1 to 3·6 lbs of nitrogen with the blue-green algae. Schleering and Laurent[10] show similar gains in soil nitrogen. Watanabe[11] has reported a gain of 780 lbs of nitrogen per acre by Tolypothrix tenuis. De[4], Fogg[3] and Williams and Burris[12] believe that blue-green algae may be of some importance in contributing to the fertility of certain tropical soils and some types of fresh water.

Pearsall[13] observed blue-green algae frequently in abundance in fresh water, specially in neutral and alkaline waters, with a relatively high content of organic matter and low content of nitrate. Bristol Roach[14] found that generous dressings of farmyard manure increased the number of blue-green algae as compard to the unmanured soil. Phosphate and calcium supply appear to be important factors for the growth of algae[15]. Gains in nitrogen were observed in rice soil on applying $CaCO_3$ and K_2HPO_4[16].

Gupta[17] have observed that organic matter is far more effective than blue-green algae in increasing the soil fertility. Pfeiffer *et al*[18] and Peterson[19] believe that algae grow mainly on the soil surface and hence do not contribute much towards soil fertility.

Taking into consideration the above cited literature the authors thought it necessary to lay certain experiments for quantitatively understanding the role of algae in nitrogen fixation. Nitrogen fixation by algae, Anabaena naviculoides and Tolypothrix tenuis, was compared with the fixation of nitrogen by organic matter and phosphate. Moreover, nitrogen fixation by algae in presence of wheat straw and Tata basic slag was also studied.

Experimental

200 gms of Allahabad loam after passing through 60 mesh sieve was taken in 500 ml flasks. 1% carbon as wheat straw and 0·25% P_2O_5 as Tata basic slag was introduced when required. Algae, Anabaena naviculoides and Tolypothrix tenuis were inoculated wherever necessary. 40% moisture was maintained throughout the experimental period. Two similar sets were arranged, one was exposed to light of a 500 watt electric bulb and the other was placed beside it covered by a thick black cloth. After 100, 200 and 300 days, composite samples were taken out and analysed for total carbon, total nitrogen, ammoniacal and nitrate nitrogen and amino acids. Amino acids were detected by paper chromatography.

The following medium was used for the growth of Anabaena naviculoides and Tolypothrix tenuis.

KNO_3	0·2 gm	K_2HPO_4	0·2 gm
$MgSO_4 7H_2O$	0·2 gm	$CaCl_2$	0·1 gm
$FeCl_3$ (1%)	3 drops	Distilled water	1000 ml.

Analysis of Allahabad loam, wheat straw and Tata basic slag

% Analysis	Soil	Wheat straw	Tata basic slag
Moisture	3·26	—	—
Loss on ignition	4·6731	91·0165	—
HCl insoluble	76·185	6·1286	22·5421
Sesquioxide	8·1361	1·4296	33·7432
Fe_2O_3	3·1689	0·6682	17·7816
Al_2O_3	—	—	15·9622
CaO	1·8592	0·6554	22·4236
MgO	1·5324	0·1376	4·0426
P_2O_5	0·2386	0·4903	7·9238
K_2O	1·1476	0·7788	0·9158
Available P_2O_5	0·0279	—	4·0724
Total carbon	0·9458	38·1643	—
Total Nitrogen	0·0775	0·5902	—
NH_3—N	0·0028	—	—
NO_3—N	0·0053	—	—
pH	7·45	—	—

The amino acids identified have been abbreviated as follows :

Gly for Glycine	Ar for Arginine.
Al for Alanine	Hi for Histidine.
Va for Valine	Glu for Glutamic acid.
Se for Serine	Asp for Aspartic acid.
Ly for Lysine	Leu for Leucine.
As for Asparagine	Pro for Proline.

[428]

TABLE 1

200 gms of soil alone   Av. Temp. 30°C

Period of exposure in days	Total carbon (gm)	Total nitrogen (gm)	NH₃—N (gm)	NO₃—N (gm)	Efficiency	Amino acids detected

NH_3—N (gm), NO_3—N (gm)

Exposed

Period of exposure in days	Total carbon (gm)	Total nitrogen (gm)	NH_3—N (gm)	NO_3—N (gm)	Efficiency	Amino acids detected
0	1·8616	0·1550	0·0056	0·0106	–	Al, Glu.
100	1·7441	0·1570	0·0062	0·0116	13·6	Al, Glu, Va.
200	1·6480	0·1582	0·0067	0·0122	13·1	Al, Glu, Va, Gly.
300	1·6039	0·1574	0·0065	0·0120	–	Al, Glu, Va, Gly.

Covered

0	1·8916	0·1550	0·0056	0·0106	–	Al, Glu.
100	1·7865	0·1560	0·0060	0·0111	9·5	Al. Glu.
200	1·7182	0·1566	0·0062	0·0114	9·2	Al, Glu.
300	1·6871	0·1561	0·0061	0·0112	–	Al, Glu, Va.

TABLE 2

200 gms of soil + 1% carbon as wheat straw

Exposed

0	3·8916	0·1859	0·0056	0·0106	–	Al, Glu.
100	3·1932	0·2049	0·0085	0·0159	27·2	Al, Glu, Va, Leu.
200	2·7585	0·2160	0·0103	0·0193	26·2	Al, Glu, Va, Leu, Asp
300	2·4688	0·2146	0·0098	0·0186	–	Al, Glu, Va, Leu. Asp Ar, Ly.

Covered

0	3·8916	0·1859	0·0056	0·0106	–	Al, Glu.
100	3·4046	0·1935	0·0077	0·0141	15·6	Al, Glu, Va.
200	3·0894	0·1981	0·0092	0·0165	15·2	Al, Glu, Va, Leu.
300	2·8531	0·1973	0·0089	0·0160	–	Al, Glu. Va, Leu, Asp, Ar.

TABLE 3

200 gms soil + 1% carbon as Wheat straw + 0·25% P_2O_5 as Tata basic slag

Exposed

0	3·8916	0·1859	0·0056	0·0106	–	Al, Glu.
100	3·0861	0·2228	0·0097	0·0189	45·8	Al, Vlu, Va, Leu, Asp
200	2·6164	0·2434	0·0131	0·0236	45·1	Al, Glu, Va, Leu, Gly, Asp, Ar.
300	2·3045	0·2416	0·0125	0·0228	–	Al, Glu, Va, Leu, Gly, Ar, Ly, As, Hi.

Covered

0	3·8916	0·1859	0·0056	0·0106	–	Al, Glu.
100	3·3148	0·1998	0·0087	0·0157	24·1	Al, Glu, Va, Leu.
200	2·9777	0·2074	0·0109	0·0194	23·6	Al, Glu, Va, Leu, Gly, Ar.
300	2·7286	0·2064	0·0105	0·0189	–	Al, Glu, Va, Leu, Gly, Ar, Hi.

TABLE 4

200 gms af soil + Anabaena   Av. Temp. 30°C

Period of exposure in days	Total carbon (gm)	Total nitrogen (gm)	NH₃—N (gm)	NO₃—N (gm)	Efficiency	Amino acids detected
			Exposed			
0	1·8916	0·1550	0·0056	0·0106	—	Al, Glu.
100	1·7694	0·1586	0·0060	0·0113	29·5	Al, Glu, Va, Asp.
200	1·6907	0·1604	0·0064	0·0118	26·9	Al. Gly, Va, Asp.
300	1·6430	0·1596	0·0063	0·0117	—	Al, Glu, Va, Asp, Se.

TABLE 5

200 gms soil + 1% carbon as wheat straw + Anabaena

0	3·8916	0·1859	0·0056	0·0106	—	Al, Glu.
100	3·3466	0·2103	0·0082	0·0153	48·4	Al, Glu, Leu, Asp, Se.
200	2·9388	0·2278	0·0098	0·0182	43·9	Al, Glu, Leu, Asp, Se, Ar. Pro.
300	2·6371	0·2262	0·0093	0·0175	—	Al, Glu, Leu, Asp, Se, Ar, Ly, Pro.

TABLE 6

200 gms soil + 1% cabon as wheat straw + 0·25% P₂O₅ as Tata basic slag + Anabaena

Exposed

0	3·8916	0·1859	0·0056	0·0106	—	Al, Glu.
100	3·2483	0·2312	0·0092	0·0181	70·4	Al, Glu, Va, Leu, Asp, Se.
200	2·8129	0·2576	0·0124	0·0223	66·5	Al, Glu, Va, Leu, Asp, Se, Ar, Pro.
300	2·4888	0·2557	0·0120	0·0217	—	Al, Glu, Leu, Asp, Se, Ar, As, Hi, Pro.

TABLE 7

200 gms soil + Tolypothrix

Exposed

0	1·8916	0·1550	0·0056	0·0106	—	Al, Glu.
100	1·7725	0·1590	0·0062	0·0116	33·6	Al, Glu, Asp, Se.
200	1·6958	0·1610	0·0069	0·0123	30·6	Al, Glu, Asp, Se.
300	1·6500	0·1601	0·0067	0·0121	—	Al, Glu, Asp, Se.

TABLE 8

200 gms soil + % carbon as wheat straw + Tolypothrix

Exposed

0	3·8916	0·1859	0·0056	0·0106	—	Al, Glu.
100	3·3993	0·2116	0·0088	0·0159	52·2	Al, Glu, Asp, Se, Va.
200	2·9550	0·2302	0·0107	0·0189	47·3	Al, Glu, Leu, Asp, Se, Pro.
300	2·6542	0·2284	0·0105	0·0182	—	Al, Glu, Leu, Asp, Se, Ar, Pro.

TABLE 9

200 gms soil + 1% carbon as wheat straw + 0·25% P_2O_5 as Tata basic slag + Tolypothrix　　　　Av. Temp. 30°C

			Exposed			
0	3·8916	0·1859	0·0056	0·0106	–	Al, Glu.
100	3·2507	0·2329	0·0097	0·0190	47·5	Al, Glu, Va, Asp Se.
200	2·8305	0·2606	0·0130	0·0237	70·4	Al, Glu, Va, Leu, Asp, Se, Ar, Pro.
300	2·5067	0·2585	0·0127	0·0229	–	Al, Glu, Leu, Asp, Se, Ar, Hi, Pro.

Discussion

A perusal of the results recorded in Table 1–3 reveals that wheat straw when added to the soil undergoes slow oxidation on soil surface in presence of air and moisture and fixes atmospheric nitrogen. Carbon oxidation and nitrogen fixation are markedly enhanced in the systems phosphated with Tata basic slag. The increase in carbon oxidation seems to be due to its alkaline nature. The increase in nitrogen fixation is due to the formation of comparatively stable phosphoproteins by phosphate supplied by Tata basic slag. Moreover the oxidation of carbon as well as the efficiency of nitrogen fixation are always greater in the systems exposed to light than that of the sets kept covered by black cloth.

The total available nitrogen and the number of amino acids is appreciably enhanced in the systems receiving straw and phosphate. Greater number of amino acids in the systems containing straw may be partly from the nitrogen fixed and partly due to the hydrolysis of straw protein. It is fascinating to note here that slag favours the formation of basic amino acids like lysine, arginine and histidine.

A careful examination of the results (vide tables 1–9) indicate that Anabaena naviculoides as well as Tolypothrix tenuis fix atmospheric nitrogen in the systems exposed to light, Tolypothrix being a better nitrogen fixer than Anabaena. No fixation of nitrogen by algae however was observed in the systems kept covered by black cloth. Though nitrogen fixed by alage as compared to organic materials and phosphate was small yet fixation of nitrogen by Anabaena as well as Tolypothrix was greatly enhanced in presence of wheat straw and basic slag. The summarised results of the nitrogen fixed by algae after 200 days of exposure are recorded in Table 10.

TABLE 10

Nitrogen fixed (mg) by algae

	Anabaena	Tolypothrix
Soil	2·2	2·8
Soil + Wheat straw	11·8	14·2
Soil + Wheat straw + Slag	14·2	17·7

From these results it can easily be concluded that wheat straw as well as basic slag when added to soil greatly enhance the growth of algae and, thereby, the nitrogen fixation. It is interesting to record here that saving of carbon results in all the systems inoculated with algae ; the saving being slightly pronounced in the systems having Tolypothrix than that of the systems having Anabaena. This again shows that the growth of algae is enhanced by carbonaceous material and phosphate. Other workers also have reported increased growth of algae in presence of different organic materials[13,14] and phosphates[15,16].

Efficiency *i.e.* the amount of nitrogen fixed in milligrams per gram of carbon oxidised is always maximum at 100 days with different treatments and is recorded in table 11.

TABLE 11

Efficiency of nitrogen fixation (mg N/gram carbon oxidised)

	Uninoculated	Inoculated Anabaena	Tolypothrix
Soil	13·6	29·5	33·6
Soil + Wheat straw	27·2	48·4	52·2
Soil + Wheat straw + Slag	45·8	70·4	74·5

The foregoing results clearly show that the efficiency of nitrogen fixation is always higher in the systems inoculated with algae than that of the uninoculated systems ; the efficiency of nitrogen fixation by Tolypothrix being greater than Anabaena.

Curiously enough, the efficiency of nitrogen fixation finds a slow fall in the next 100 days while in the algal systems the fall is abrupt.

Moreover, serine and proline appear frequently in the algal systems in addition to alanine, valine, glutamic acid, aspartic acid, lysine, leucine and histidine. Thus serine and proline seem to result from the exudates of algae.

Hence from the above data and discussion the following conclusions are made:

1. Anabaena naviculoides as well as Tolypothrix tenuis fix atmospheric nitrogen, Tolypothrix being a better fixer than Anabaena.

2. The nitrogen fixed by algae is small as compared to that of nitrogen fixed by organic matter and slag.

3. The growth of algae and, thereby, the nitrogen fixed is considerably enhanced in presence of wheat straw and Tata basic slag.

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Effect of time on the Hydrolysis of some Naturally Occurring Rock phosphates, Basic slags and Superphosphate

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Abstract

It has been observed that the hydrolysis of Trichinopoly, Bihar and Algerian rock phosphates and Tata, Kulti, German and Belgian basic slags continues for many days. Hence, when basic slags or naturally occurring rock phosphates will be applied to soil, they can maintain a fairly constant supply of phosphoric acid in solution for efficient growth of plants. The results further show that superphosphate is highly soluble in water, therefore, it will be superior to basic slags or naturally occurring rock phosphates in the conditions where plants need immediately supply of phosphorus.

Introduction

Solubility and hydrolysis of a compound are of fundamental importance which govern its isolation and occurrence in nature. From the point of view of the availability of phosphates to plants, solubility and hydrolysis in water play an important role. Phosphorus is absorbed by plants chiefly as orthophosphate ion. A characteristic feature of phosphate absorption by plants from soils is the ability of plant to accumulate and maintain a high concentration of inorganic phosphates within its tissues despite the low concentration of phosphate ion in soil solution. It is obvious that in order to derive an adequate supply of phosphate from a low phosphate concentration soil repeated restoration of the water soluble phosphate seems necessary. The water soluble phosphate in the soil has to be in equilibrium with the phosphate in the solid state. If an adequate stock of phosphate is maintained in the soil, the speed with which equilibrium between the soil and liquid phase is attained can be considered as an indication of the capacity of the soil for providing phosphorus to crops.

The direct use of mineral phosphates in finely ground form was first advocated by Elie de Beaumont[1] in 1856 and since then a number of agronomists and agriculturists[2-1] working in different parts of the world have recommended the application of finely ground unacidulated raw rock phosphate directly to the field and obtained better crop yields. Wagner[5] in Germany and Wrightson and Munrion[6] in England experimented with finely ground basic slags in about 1884 and showed that they had a striking influence upon crops, especially those of the leguminous order. Russell[7] stated that superphosphate which is more costly than basic slag is more effective than basic slag in the first year but not always in subsequent years in light soils. Barnes[8], Fried[9], Cullen[10], Cooke[11] and Truog[2] have reported basic slag to have an efficiency of 40 per cent of that of superphosphate when applied under the same conditions. But on the other hand, Noll,

Irwin and Gardner[13] at Pennsylvania Experimental Station have observed after 12 years that basic slag is superior to superphosphate and bone meal. Whittakar[14] and Vanderford[15] obtained marked beneficial effects of basic slags in plant growth. Murray[16] and Charlon[17] have found that basic slag rich in phosphate is as good as superphosphate and can be used as a source of lime and phosphate. Williams and Custon[18] obtained remarkable beneficial effects of basic slags in plant growth.

In this paper an attempt has been made to study the effect of time on the hydrolysis of Trichinopoly, Bihar and Algerian rock phosphates, Tata, Kulti, German and Belgian basic slags and superphosphate.

Experimental

1. *Sample* : The composition of rock phosphates and basic slags utilised in these experiments is the same as described in the paper[19] dealing with the influence of temperature on the hydrolysis of these materials. Superphosphate used in these experiments contained 18·63% P_2O_5 and 22·78% CaO.

2. *Solubility determinations* : 1·00 gm of the rock phosphates, basic slags or superphosphate, sieved through a 200 mesh sieve was taken in Jena glass bottles and 100 ml of distilled water was added to it. The bottles were kept in a thermostat maintained at a temperature of 30°C. The contents of the bottles were stirred daily. Different sets were used for different intervals of time. After definite intervals of time the bottles were taken out of the thermostat and shaken for one hour in a mechanical shaker and allowed to stand for some time. The contents were then filtered. Aliquot portions were utilised for determining P_2O_5[20,21], lime [20], pH and electric conductivity.

A portable Cambridge pH meter and "Leitfahigkeitsmesser" magic eye conductivity bridge (Laboratory model S. No. 177) were utilized for pH and conductivity determinations respectively.

Results

TABLE 1

Number of days 50

Material	Millimoles per litre		pH	Specific conductivity in mhos × 10⁻⁴
	P_2O_5	CaO		
Tata basic slag	0·0698	1·8525	8·75	3·42
Kulti basic slag	0·0371	2·8449	9·15	5·38
German basic slag	0·1535	2·4041	8·90	6·60
Belgian basic slag	0·1415	2·3623	8·70	5·66
Trichinopoly rock phosphate	0·0993	0·8085	8·00	2·43
Bihar rock phosphate	0·1331	0·4889	7·85	2·85
Algerian rock phosphate	0·1559	0·5427	7·75	3·22
Superphosphate	10·1524	13·2006	3·55	36·18

| Material | Millimoles per litre | | pH | Specific conductivity in mhos × 10⁻⁴ |
	P_2O_5	CaO		

Number of days 100

Material	P_2O_5	CaO	pH	Specific conductivity in mhos × 10⁻⁴
Tata basic slag	0·0803	2·3011	8·95	4·28
Kulti basic slag	0·0448	3·5665	9·30	6·40
German basic slag	0·1780	2·9074	7·00	7·33
Belgian basic slag	0·1636	2·7984	8·85	7·04
Trichinopoly rock phosphate	0·1123	0·9823	8·10	2·82
Bihar rock phosphate	0·1475	0·5628	7·95	3·64
Algerian rock phosphate	0·1723	0·5966	7·90	3·91
Superphosphate	10·5304	13·8422	3·55	37·20

Number of days 150

Material	P_2O_5	CaO	pH	Specific conductivity in mhos × 10⁻⁴
Tata basic slag	0·0854	2·7081	9·05	4·70
Kulti basic slag	0·0495	4·0313	9·35	6·82
German basic slag	0·1938	3·3240	9·10	7·64
Belgian basic slag	0·1998	3·2239	8·95	7·73
Trichinopoly rock phosphate	0·1295	1·0991	8·15	3·05
Bihar rock phosphate	0·1627	0·6537	8·00	3·95
Algerian rock phosphate	0·1902	0·6775	8·05	4·75
Superphosphate	10·8006	14·2611	3·60	38·16

Number of days 200

Material	P_2O_5	CaO	pH	Specific conductivity in mhos × 10⁻⁴
Tata basic slag	0·0849	2·6617	9·05	4·59
Kulti basic slag	0·0518	4·4081	9·40	6·92
German basic slag	0·2006	3·8120	9·25	8·02
Belgian basic slag	0·1891	3·1019	8·95	7·57
Trichinopoly rock phosphate	0·1406	1·1525	8·20	3·38
Bihar rock phosphate	0·1771	0·7393	8·10	4·45
Algerian rock phosphate	0·2339	0·7672	8·10	5·36
Superphosphate	10·9975	14·5043	3·60	39·02

Number of days 250

| Material	P_2O_5	CaO	pH	Specific conductivity in mhos × 10⁻⁴
Tata basic slag	0·0785	2·5516	9·10	4·48
Kulti basic slag	0·0499	4·1869	9·45	6·80
German basic slag	0·1885	3·6551	9·25	7·52
Belgian basic slag	0·1802	2·8697	9·00	7·11
Trichinopoly rock phosphate	0·1400	1·1903	8·25	3·69
Bihar rock phosphate	0·1617	0·7 51	8·10	4·36
Algerian rock phosphate	0·2163	0·7402	8·15	5·27
Superphosphate	11·0854	14·6218	3·65	39·90

Discussion

The experimental results recorded in Table 1 clearly show that the hydrolysis of sparingly soluble basic slags and naturally occurring rock phosphates continues for many days. The solubility of Tata and Belgian basic slags increases maximum upto 150 days and of Kulti and German basic slags and Trichinopoly, Bihar and Algerian rock phosphates increases upto 200 days and afterwards there is a fall in the values. These results are supported by electric conductivity measurements. It may be due to the fact that the aqueous solutions of rock phosphates and basic slags contain Mg^{++}, Ca^{++}, HPO_4^{--}, PO_4^{---} and OH^- ions and it is probable that in the course of time basic phosphates are likely to be formed which are less soluble than original phosphates resulting in the partial removal of OH^- ions and thereby decreasing the conductivity and solubility. The decrease in solubility may also be due to the adsorption of the released phosphate ions by the oxides of iron and aluminium. In all these experiments the maximum time allowed was 250 days and if more time is allowed these absorbed ions may again be released into the solution due to the ageing phenomenon.

The pH of the aqueous solutions of basic slags and rock phosphates increases with lapse of time indicating that more of lime than phosphoric acid passes into the solution. This is in agreement with the solubility results.

Superphosphate is highly soluble in water. The amounts of P_2O_5 and CaO passing into the solution with 1 per cent superphosphate are 9·3200 and 12·0162 millimoles per litre respectively and the pH and conductivity of the aqueous solution of superphosphate is 3·50 and 36·40 × 10^{-4} mhos respectively[22]. It appears that the high solubility of superphosphate is due to the presence of monocalcium phosphate in superphosphate which is water soluble. The results show that there are no significant changes in the solubility, pH and electric conductivity of the aqueous solution of superphosphate with the increase in the number of days. As the resulting solution of superphosphate is highly acidic, there has been a considerable controversy regarding the power of superphosphate in increasing the acidity of the soil. When superphosphate is added to acidic soils or soils poor in humus containing soluble salts of iron, aluminium and titanium, superphosphate is likely to react according to the following equations :

$$Ca(H_2PO_4)_2 + Fe_2(SO_4)_3 = 2FePO_4 + CaSO_4 + 2H_2SO_4$$

$$Ca(H_2PO_4)_2 + Al_2(SO_4)_3 = 2AlPO_4 + CaSO_4 + 2H_2SO_4$$

$$2Ca(H_2PO_4)_2 + 3TiCl_4 = Ti_3(PO_4)_4 + 2CaCl_2 + 8HCl$$
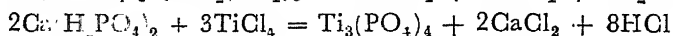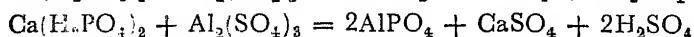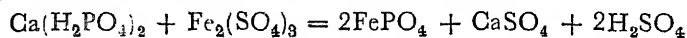
It is clear, therefore, that in such soils the liberation of mineral acids makes the soil more acidic and their lime requirement increases markedly. This explains the viewpoint of workers who have reported an increase in the acidity of the soil by fertilizing with superphosphate. On the other hand, when superphosphate is added to neutral or slightly alkaline soils containing calcium carbonate, there is formation of a mixture of sparingly soluble di- and tri- calcium phosphates according to the following equations :

$$Ca(H_2PO_4)_2 + 2CaCO_3 = Ca(HCO_3)_2 + 2CaHPO_4$$

$$Ca(H_2PO_4)_2 \, 2CaCO_3 = Ca_3(PO_4)_2 + 2H_2O + 2CO_2$$
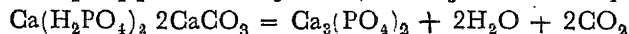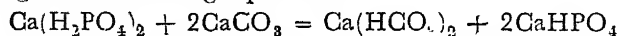
Hence, in these processes small amounts of calcium, i.e. equivalent to calcium introduced in superphosphate as monocalcium phosphate may be washed away as calcium bicarbonate when rain falls. Consequently, under these conditions the lime requirement of such a soil may increase temporarily. The newly formed di- and tri- calcium phosphates much more soluble than the phosphates in

the soil. Therefore, superphosphate can more readily supply available phosphates to plants than naturally occurring phosphate rocks or basic slags.

It is evident from these results that basic slags and rock phosphates can maintain a fairly constant supply of phosphorus and lime. These materials will be more efficient for the growth of plants than highly soluble superphosphate and its use may not be necessary as it gets converted to more insoluble form of phosphate classed in the unavailable group by reacting with some soil constituents. Due to the high solubility of superphosphate, it will be superior to rock phosphates or basic slags in the conditions where plants need immediate supply of phosphorus.

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Influence of Phosphates on the Transformations of Carbon and Nitrogen during the composting of Municipal rubbish

By

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The sanitary reclamation and utilization of nutrients in wastes can be an important factor in improving the nutrition, health and economic status of a person. The return of the nutrients in wastes from the cities to improve agricultural production is of vital importance to all nations.

It is estimated that about one fourth of the food and fibre produced in the world is wasted as municipal garbage and waste. Taking the world production of food and fibre at 2000 million tons, the waste and garbage comes to 500 million tons containing approximately 10 million tons of nitrogen. The garbage and waste also contains potash, lime, magnesia, phosphoric acid and trace elements as well. The carbonaceous compounds when incorporated in soils under favourable conditions can fix atmospheric nitrogen when reinforced with phosphatic materials like basic slag, rock phosphate and superphosphate. Thus if this waste is properly preserved and managed for nitrogen fixation it can supply 20 million tons of nitrogen. 10 million tons of phosphoric acid and about 20 million tons of potash.

Dhar in his Presidential address to the National Academy of Sciences, India in the year 1952 has stated that our composting experiments convince us that calcium phosphate is useful in composting of plant materials, especially in the absence of nitrogenous fertilizers, because phosphates help in nitrogen fixation in the slow oxidation of organic matter and hence calcium phosphate or rock phosphate should be largely used in composting.

Nilsson[9] reported that liming and manuring increased P uptake, and superphosphate mixed with manuring increased P uptake still further in unlimed soil.

Doring[1] reported that farm yard manure fermented with phosphate increaed the yield of crops upto 20% as campared with the yields obtained by unfermented composts.

Acharya[1], Thorne[15] and Karraker[7] obtained good crops when they applied phosphate fermented composts.

Dhar, Bose and Gaur[3], Gupta[6], Pandey[11], Sharma[12] and Srivastava[14] in their experiments on the composting of different organic materials like animal dung, straw, water hyacinth, cactus, municipal rubbish have shown that the incorporation of powdered rock phosphate or basic slags or a mixture of powdered rock phosphate and superphosphate is highly beneficial due to the increased fixation of atmospheric nitrogen in these composts in presence of phosphates.

In order to study the influence of phosphates on the transformations of carbon and Nitrogen during the composting of municipal rubbish, an experiment was conducted in 1965-66. The composting of municipal rubbish was carried on the ground of Sheila Dhar Institute of Soil Science, University of Allahabad

Six rectangular heaps of municipal rubbish approximately of the dimension of 10' × 5' × 3' were made on the surface of the soil in the last week of September, 1965. One heap was left as such and in the remaining 5 heaps 4 types of slags *viz*. Tata, Kulti, Durgapur and German and Single superphosphate at the rate of 9 Kgms P_2O_5 per 3 tonnes of municipal rubbish was added and mixed well. After regular intervals samples were taken out for determining Carbon, Nitrogen and other ingredients.

The results obtained after 150 days of composting are recorded :

Carbon and Nitrogen content of composts prepared in heaps after 150 days

S. no.	Treatments	Initial carbon %	Carbon unoxidis- ed %	Carbon oxidised %	Initial Total nitrogen %	Total nitrogen %	Total nitrogen fixed %
1.	Municipal rubbish only	14·4028	6·2000	8·2028	0·6022	0·8260	0·2238
2.	Municipal rubbish + Tata basic slag.	14·4028	4·6015	9·8013	0 6022	1·0416	0·4394
3.	Municipal rubbish + Durgapur basic slag.	14·4028	4·8016	9·6012	0·6022	0·9800	0·3778
4.	Municipal rubbish + Kulti basic slag.	14·4028	4·5018	9·9010	0·6022	0·9828	0·3806
5.	Municipal rubbish + German basic slag.	14·4028	4·3200	10·0828	0·6022	1·0600	0·4578
6.	Municipal rubbish + single superphosphate.	14·4028	4·9530	9·4498	0·6022	0·9906	0·3884

The foregoing results clearly show that there is marked oxidation of carbonaceous compounds when municipal rubbish is allowed to come in contact with air in solar light. This oxidation further enhances when phosphatic materials like basic slag and single superphosphate are mixed with municipal rubbish. Basic slags (Tata, Durgapur, Kulti and German) were found more effective in increasing the oxidation than single superphosphate. This appears to be due to the fact that basic slags are alkaline and that alkalinity favours oxidation has been established by the past 30 years work of Dhar. Trace elements present in the basic slags also help in oxidation. Gupta[6] has observed that addition of trace elements alongwith different phosphates increases the oxidation of carbon. Waksman and Tenney[16] have reported considerable losses of organic matter in composting. Norman[10] found that in 4 days, 10 gm of hemicellullose and 1 gm of cellulose were lost during the rotting of 100 gm of oat straw containing 23 % free hemicellulose and 44% pure cellulose. Martin and Wang[3] have observed 80 % reduction of organic matter which shows the rapidity with which it gets oxidised.

During the slow oxidation of municipal rubbish, a progressive increase in Nitrogen concentration has been observed. The increase in Nitrogen is pronounced in the systems containing phosphates. Thus increase is due evidently to fixation of atmospheric nitrogen and also partially due to rapid and continuous losses of organic matter.

The increase in nitrogen during the decomposition and oxidation of organic materials has been reported by number of workers, Gotaas and Coworkers[5], Singh[13], Gupta[6] Dhar and Ghildayal[2], Pandey[11], Sharma[12] and Srivastava[14].

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A comparative study of Grasses and Legumes when Ploughed-in in the soil in presence and absence of Phosphates and Tolypothrix in Crop-production

By

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Abstract

Grasses *viz.* Paragrass, rhodegrass and legumes *viz.* lucerne and dhaincha were grown on sandy loam soils of Allahabad and after 6 months the whole crop was ploughed-in in the soil. Soils in which grasses were ploughed-in with phosphates were found to be rich in nutrient content than the plots ploughed-in with legumes. Two months time was given for the decomposition of the ploughed-in crops and a paddy crop was transplanted, wherever required Tolypothrix tenuis was also inoculated in the plots.

It was observed that increase in the yield was higher in plots in which grasses with phosphates were ploughed-in than that of legume plots and there was very small increase in yield due to the algal inoculation in comparison to that obtained from the plots containing a mixture of organic materials and phosphates.

Dhar[1, 2, 3] has established that when organic materials with C/N ratio greater than 10 are applied and allowed to undergo oxidation the energy obtained by the oxidation of carbonaceous compounds is utilised in fixing the nitrogen of the atmosphere and synthesis of proteins and in this process sunlight is actually utilised in improving the nitrogen status of soils all over the world. White and his associates[4] in their experiment found that with 20 plots soils under continuous cultivation of permanent grass, the unfertilized grass land (1869–1940) show a nitrogen level of 68·2% above the control plot soils and 42·1% above NPK treatment. Russell[5] has also reported that nitrogen content of a grass land increased from 0·152% in 1856 to 0·338% in 1912.

From time immemorial the turning under of a green crop to better the condition of soil has been a common practice. The general practice is to turn into the soil undecomposed green plant tissue, usually legume crops, because nodule bacteria fix some amount of nitrogen and at the same time by the process of decomposition of plant residues nitrogen content of the soil is increased. In some tropical countries grasses have shown better effect on the fertility status of the soils than that of legume crops.[6]

Keeping the above cited literature in view, some field trial experiments were conducted to study the comparative influence of grasses and legumes when they are ploughed into the soil, in absence and presence of phosphates and Tolypothrix tenuis, on crop-production and soil fertility.

[441]

Experimental

Field trials were conducted at Village Fatuha, Allahabad in an area where land is fairly uniform and which is under cultivation since a long time. The structure of soil is sandy loam. Soil samples were taken out from different layers and from different spots upto the depth of 6 inches in order to determine the uniformity of the soil of the field. They were analysed for its constituents. The legume crops *viz.* lucerne and berseem and grasses *viz.* paragrass and rhodegrasses were grown along with 50 lbs of P_2O_5 application of Tata basic slags.

After six months growth the legume crops, and after eight months the grasses were ploughed into the soil and a sufficient time were given for the decomposition of the crops and then the soils in plots were analysed for its different constituents. A paddy crop was transplanted and after the harvest of crop, the yield of grain and straw were tabulated. The soil after the harvest was also analysed to determined the residual effect of the green manure crops in the soil. Tolypothrix tenuis was also inoculated in the plots wherever it was necessary.

Detail lay out of the plan

1. Soil alone
2. Soil + Berseem
3. Soil + Lucerne
4. Soil + Rhodegrass
5. Soil + Paragrass
6. Soil + Berseem + P_2O_5
7. Soil + Lucerne + P_2O_5
8. Soil + Rhodegrass + P_2O_5
9. Soil + Paragrass + P_2O_5
1. Size of the plot = 1/60th acre.
   No. of application = 6
   Total No. of treatments 9 × 6 = 54 plots.

TABLE 1

		Soil	TBS
1.	Loss on ignition	4·3614	–
2.	HCl insoluble	80·4917	16·2361
3.	Sesquioxide	8·1264	–
4.	Fe_2O_3	2·4569	15·2416
5.	Total P_2O_5	0·1700	7·1625
6.	Available P_2O_5	0·0107	–
7.	Total K_2O	0·4623	0·6501
8.	Total MgO	0·3644	4·7938
9.	Total CaO	1·0461	38·7905
10.	Total Carbon	0·4963	
11.	Total Nitrogen	0·0476	
12.	NH_3—N	0·0017	
13.	NO_3—N	0·0024	
14.	C/N ratio	10·4	

Results and Discussions

TABLE 2
Analysis of soil samples before ploughing in of the legume and grasses

Treatments	Total carbon	Total nitrogen	Avail. N	Total P_2O_5	Avail. P_2O_5
1. Soil alone	0·4963	0·0476	0·0041	0·1700	0·0107
2. Soil + Berseem	0·4762	0·0493	0·0065	0·1641	0·0102
3. Soil + Lucerne	0·4793	0·0490	0·0063	0·1639	0·0100
4. Soil + Paragrass	0·4569	0·0437	0·0037	0·1637	0·0094
5. Soil + Rhodegrass	0·4506	0·0458	0·0035	0·1635	0·0092
6. Soil + Berseem + P_2O_5	0·4638	0·0514	0·0072	0·1805	0·0116
7. Soil + Lucerne + P_2O_5	0·4507	0·0503	0·0069	0·1800	0·0119
8. Soil + Paragrass + P_2O_5	0·4520	0·0442	0·0038	0·1794	0·0114
9. Soil + Rhodegrass+P_2O_5	0·4493	0·0434	0·0039	0·1792	0·0116

TABLE 3
Analysis of soil samples after ploughing in of the crops (i.e. before transplanting of paddy)

1. Soil alone	0·4955	0·0479	0·0045	0·1665	0.0100
2. Soil + Berseem	0·7809	0·0738	0·0094	0·1768	0·0109
3. Soil + Lucerne	0·7958	0·0764	0·0097	0·1759	0·0108
4. Soil + Paragrass	0·8178	0·0720	0·0052	0·1748	0·0110
5. Soil + Rhodegrass	0·8095	0·0729	0·0057	0·1757	0·0114
6. Soil + Berseem + P_2O_5	0·6408	0·0857	0·0103	0·1942	0·0127
7. Soil + Lucerne + P_2O_5	0·6259	0.0869	0·0107	0·1947	0·0132
8. Soil + Paragrass + P_2O_5	0·6785	0·0865	0·0110	0·1952	0·0141
9. Soil + Rhodegrass+P_2O_5	0·6538	0·0874	0·0114	0·1950	0·0145

TABLE 4
Average yield of paddy grain and straw Kgs. per plot (Average of 3 plots)

	Treatments	Paddy grain	Paddy straw
1.	Soil alone	9·5	17·6
2.	Soil + Berseem	13·5	24·0
3.	Soil + Tolypothrix	10·4	20·1
4.	Soil + Berseem + Toly.	14·6	25·5
5.	Soil + T.B.S.	11·4	21·2
6.	Soil + Berseem + T.B.S.	17·0	30·0
7.	Soil + T.B.S. + Toly. + Berseem	18·4	32·5
8.	Soil + Lucerne	13·0	22·8
9.	Soil + Lucerne + Toly.	14·2	24·9
10.	Soil + Lucerne + T.B.S.	16·8	28·8
11.	Soil + Lucerne + T.B.S. + Toly.	18·1	31·6
12.	Soil + Paragrass	12·7	20·7
13.	Soil + Paragrass + Toly.	13·9	22·3
14.	Soil + Paragrass + T.B.S.	17·5	31·1
15.	Soil + Paragrass + T.B.S. + Toly.	18·9	33·2
16.	Soil + Rhodegrass	12·9	22·2
17.	Soil + Rhodegrass + Toly.	14·0	23·4
18.	Soil + Rhodegrass + T.B.S.	17·8	31·9
19.	Soil + Rhodegrass + T.B.S. + Toly.	19·2	34·5

TABLE 5
Analysis of soil sample after harvest of paddy crop

Treatments	Total carbon %	Total nitrogen %	Available N	Total P_2O_5	Available P_2O_5
Soil alone	0·4795	0·0453	0·0037	0·1640	0·0012
Soil + Berseem	0·6978	0·0685	0·0083	0·1748	0·0114
Soil + Lucerne	0·7037	0·0690	0·0056	0·1749	0·0110
Soil + Paragrass	0·7184	0·07 3	0·0045	0·1730	0·0104
Soil + Rhodegrass	0·7093	0·0699	0·0047	0·1741	0·0109
Soil + Lucerne + P_2O_5	0·5694	0·0817	0·0096	0·1936	0·0139
Soil + Berseem + P_2O_5	0·5867	0·0806	0·0094	0·1132	0·0138
Soil + Paragrass + P_2O_5	0·5984	0·0820	0·0098	0·1941	0·0146
Soil + Rhodegrass + P_2O_5	0·6038	0·0819	0·0102	0·1939	0·0150
Soil + Tolypo.	0·4832	0·0459	0·0039	0·1641	0·0090
Soil + Berseem + Tolypo.	0·6995	0·0687	0·0085	0·1749	0·0112
Soil + Lucerne + Tolypo.	0·1707	0·0618	0·0088	0·1749	0·0108
Soil + Paragrass + Tolypo.	0·7205	0·0720	0·0049	0·1729	0·0102
Soil + Rhodegrass + Tolypo.	0·7137	0·0705	0·0051	0·1740	0·0106
Soil + Beseem + P_2O_5 + Tolypo.	0·5890	0·0809	0·0098	0·1930	0·0132
Soil + Lucerne + P_2O_5 + Tolypo.	0·5697	0·0819	0·0103	0·1935	0·0137
Soil + Paragrass + P_2O_5 + Tolypo.	0·5997	0·0827	0·0105	0·1940	0·0140
Soil + Rhodegrass + P_2O_5 + Tolypo.	0·6088	0·0820	0·0108	0·1937	0·0146

From Tables 3 and 4 the yield of paddy grain and straw have increased in plots in which grasses are ploughed-in with a basal dose of 50 lbs of P_2O_5 in form of Tata basic slag. Legumes when ploughed in enriched the nutrient status of soil but after harvest of the crop, its residual effect is not so significant as compared to the grass ploughed in plots.

The possible reason for the above fact may be due to higher organic matter incorporation into the soil by grasses than legumes. Phosphates in presence of high temperature, light and humidity increase the oxidation of carbonaceous materials thereby, releasing more energy which is helpful in fixing atmospheric nitrogen.

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Influence of blue green algae on Nitrogen Fixation in soil using Phosphates and Organic Materials

By

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Abstract

Influence of blue green algae *viz*. Tolypothrix tenuis and Anabaena naviculoides separately and in combination with the energy materials like wheat straw, sunhemp at the rate of 0·5% carbon and in phosphates like German Basic Slag as 0·5% P_2O_5 and Tata Basic Slag as 0·5% P_2O_5 were studied in Kotdwara (Garhwal) soil.

By the slow oxidation of these organic materials, there has been an increase in nitrogen which was due to the fixation of atmospheric nitrogen. In the sets inoculated with algae there was saving in the carbon and slight increase in nitrogen. It has further been observed that there was greater fixation of nitrogen when phosphates were mixed with organic materials.

Under the treatment : 250 gms. soil + 0·5% carbon as wheat straw+0·5% P_2O_5 as German Basic Slag + Tolypothrix tenuis, there was maximum nitrogen fixation in 150 days.

Experimental

A considerable amount of work has been carried out recently on the part played by blue green algae in fixing atmospheric nitrogen and thereby maintain soil fertility. Franck[1] first advanced the view that the growth of algae was responsible for the increase of nitrogen in soils exposed to light. It was also supported by Schloesing and Laurent[2], Koch and Kossowitch[3], Richter[4]. Drewes[5] observed that Anabaena can fix 2-3 mgs. of nitrogen in 250 ml. medium in two months. Allison and Morris[6] found 40 mgms of nitrogen fixed by the blue green algae per 100 ml. of nutrient solution containing 1% sucrose when exposed to sunlight. De[7], Singh[8] and others have also reported the fixation of nitrogen with bacteria free unialgal culture.

In order to throw light on this problem, we have carried out experiments with algae in Kotdwara soil (Garhwal) of U. P. Organic materials like wheat straw and sunhemp as 0·5% carbon in each case and phosphates Tata Basic slag (0·5% P_2O_5) and German Basic slag (0·5% P_2O_5) were added with 250 gms. soil in clean enamelled dishes. After mixing, two unialgal blue green namely Anabaena naviculoides and Tolypothrix tenuis were mixed and moisture content maintained at 30% level both in artificial light under 200 watt bulb and another set in dark.

Discussion

A careful examination of the result shows that both oxidation of carbon and fixation of nitrogen are enhanced by addition of phosphates (T. B. S. and G. B. S.) and always found to be greater in light than in dark.

As a result of mixing energy materials wheat straw and sunhemp in the soil both in presence and absence of phosphates, there was further increase of nitrogen in phosphate sets than in unphosphated ones.

In sets inoculated with algae there was small saving in carbon and slight increase in nitrogen was always found in light. But there was grerter fixation of nitrogen when phosphates were mixed with organic materials due to formation of stable phospho-proteins or phospho-lignoproteins, which resist nitrification and loss of nitrogen, caused by the formation and decomposition of Ammonium nitrite. $NH_4 NO_2 \rightarrow N_2 + 2H_2O + 718$ K. cals. In sets inoculated with Tolypothrix and Anabaena, there is appreciable increase in nitrogen over that of the control sets.

After 150 days, the increase in nitrogen over the initial nitrogen of the system due to the inoculation of Anabaena and Tolypothrix is 2·3 and 2·5 mgms. which is small and almost negligible in comparison to that fixed by the oxidation of organic material aided by phosphates. The value being 25·2 and 27·2 mgms. for wheat straw and 23·5 and 25·7 mgms for sunhemp in the presence of T. B. S. and G. B. S. respectively.

The efficiency of nitrogen fixation is always found to be much greater in sets inoculated with algae then those without it. With Tolypothrix the efficiency is always found to be greater than that with Anabaena because Tolypothrix being good nitrogen fixers than the Anabaena.

Another important observation is that the influence of algae is more pronounced in sets containing the energy materials and phosphates showing that these materials activate the growth of algae. The increase in nitrogen in 150 days, due to Anabaena and Tolypothrix when inoculated in soil alone is only 0·5 and 0·7 mgms. respectively over the control soils. While in presence of organic materials, wheat straw and sunhemp, so the respective incr ase is 8·8 and 8·2 mgms. in case of Anabaena and 9·8 and 9·0 mgms. in case of Tolypothrix. In presence of phosphate these values are higher. These results are in agreement with the observation of De and Sulaiman[9] ard De and Mandal[10]. Among organic materials wheat straw fixed more nitrogen than sunhemp. The fixation is always greater in light than in the dark.

A very important observation is that the available phosphates of the system increases with the oxidation of carbon and the increase is greater in the inoculated sets than in the uninoculated ones. The increase in the available phosphate by the inoculation of algae may be due to the fact that algae excreate some organic acids which might dissolve some of the phosphates. It was noticed that the maximum nitrogen fixation under the treatments 250 gms. soil + W.S. (0·5%C) + G. B. S. (0·5%P_2O_5) + Tolypothrix tenuis in light.

Thus, from these investigations it is observed that light plays a very important role in nitrogen fixation. The contribution to nitrogen increase in soil by Algae is small as campared to that of organic matter and phosphates.

The fixation of nitrogen by algae is increased in presence of organic matter and phosphates. Hence, it is conclusively proved that the addition of organic matter and phosphates markedly enhances the carbon and nitrogen status and thereby, the fertility of the soils, to a greater extent than that obtained by the Blue green algae.

The analysis of the soil and the materials used are as follows :

	Soil %	Sunhemp %	Wheat straw (W. S.) %	Tata Basic slag (T.B.S.) %	German Basic slag (G.B.S.) %
Total Carbon	0·4488	39·798	38·485	–	–
Total Nitrogen	0·04048	2·082	0·6368	–	–
Available P_2O_5	0·02098	–	–	4·0436	9·940
Total P_2O_5	0·06889	–	–	7·1402	17·460
pH.	7·7	–	–	–	–
C/N ratio	11·1	18·0	60·4	–	–

Note : G. B. S.—German Basic Slag
T. B. S.—Tata Basic Slag
W. S.—Wheat Straw

TABLE 1

Treatments		Initial carbon (gm.)	Total carbon after 150 days (gm.)	Initial nitrogen (gm.)	Total nitrogen after 150 days (gm.)	Efficiency	Initial available P_2O_5 (gm)	Available P_2O_5 after 150 days(gm)
1. Control 250 gms. soil alone	Light	1·1220	0·9420	0·1012	0·1030	10·0	0·0524	0·0537
	Dark	1·1220	1·0387	0·1012	0·1018	7·2	0·0524	0·0534
2. 250 gms. soil + Anabaena naviculoides	Light	1·1220	1·0026	0·1012	0·1035	19·2	0·0524	0·0538
	Dark	1·1220	1·0340	0·1012	0 1019	8·1	0·0524	0·0536
3. 250 gms. soil + Tolypothrix tenuis	Light	1 1220	1·0084	0·1012	0·1037	22·0	0·0524	0·0539
	Dark	1·1220	1·0260	0·1012	0·1020	8·3	0·0524	0·0535
4. 250 gms. + 0·5% P_2O_5 as T.B.S.	Light	1·1220	1·9288	0·1012	0·1035	11·9	0·7592	0·7620
	Dark	1·1220	1·0136	0·1012	0·1021	8·3	0·7592	0·7612
5. 250 gms. soil + 0·5% $P_2O_{,,}$ as T.B.S. +Anabaena naviculoides	Light	1·1220	1·0065	0·1012	0·1038	22·5	0·7592	0·7622
	Dark	1·1220	1·0084	0·1012	0·1022	8·8	0·7592	0·7613
6. 250 gms. soil + 0·5% P_2O_5 as T.B.S. + Tolypothrix tenuis	Light	1·1220	1·0076	0·1012	0·1039	23·8	0·7592	0·7623
	Dark	1·1220	1·0084	0·1012	0·1022	8·8	0 7592	0·7614
7. 250 gms. soil + 0·5% P_2O_5 as G.B.S.	Light	1·1220	0·9237	0 1012	0·1036	12·1	0·7640	0·7672
	Dark	1·1220	1·0071	0·1012	0·1022	8·7	0·7640	0·7662
8. 250 gms. soil + 0·5% P_2O_5 as G.B.S. +Anabaena naviculoides	Light	1·1220	1·0006	0·1012	0·1042	24·7	0·7640	0·7674
	Dark	1·1220	1·0025	0·1012	0·1023	9·2	0·7640	0·7663
9. 250 gms. soil + 0·5% P_2O_5 as G.B.S. + Tolypothrix tenuis	Light	1·1220	1·0009	0·1012	0·1043	25·6	0 7640	0·7675
	Dark	1·1220	1·0025	0·1012	0·1023	9·2	0·7640	0·7664
10. 250 gms. soil + 0·5% carbon as wheat straw + W.S.	Light	2·3720	1·6860	0·1217	0·1337	17·5	0·0524	0 0555
	Dark	2·3720	1·9550	0·1217	0·1267	12·0	0 0524	0·0545
11. 250 gm. soil + 0·5% carbon as W.S. +Anabaena naviculoides	Light	2·3720	1·8255	0·1217	0·1425	39·5	0·0524	0·0558
	Dark	2·3720	1·9547	0·1217	0·1270	12·7	0·0524	0·0547
12. 250 gms. soil + 0·5% carbon as W.S. + Tolypothrix tenuis	Light	2·3720	1·8403	0·1217	0·1435	41·0	0·0524	0·0562
	Dark	2·3720	1·9580	0·1217	0·1270	12·8	0·0524	0·0546
13. 250 gms. soil + 0·5% carbon as W.S. + 0·5% P_2O_5 as Tata Basic slag (T.B.S.)	Light	2·3720	1·6508	0·1217	0·1269	34·8	0·7592	0·8227
	Dark	2·3720	1·9143	0·1217	0·1292	15·8	0·7592	0·8186
14. 250 gms. soil + 0·5% carbon as W.S. + 0·5% P_2O_5 as German Basic slag (G.B.S.)	Light	2·3720	1·6268	0·1217	0·1489	36·5	0·7640	0·8348
	Dark	2·3720	1·9000	0·1217	0·1302	18·0	0·7640	0·8241

Treatments		Initial carbon (gm.)	Total carbon after 150 days (gm.)	Initial nitrogen (gm.)	Total nitrogen after 150 days (gm.)	Efficiency	Initial available P_2O_5 (gm)	Available P_2O_5 after 150 days(gm)
15. 250 gms. soil + 0·5% carbon as W.S. + 0·5% P_2O_5 as T.B.S. + Anabaena naviculoides	Light	2·3720	1·7120	0·1217	0·1534	48·0	0·7592	0·8230
	Dark	2·3720	1·9040	0·1217	0·1314	20·7	0·7592	0·8200
16. 250 gms. soil + 0·5% carbon as W.S. + 0·5% P_2O_5 as T.B.S + Tolypothrix tenuis	Light	2·3720	1·7100	0·1217	0·1545	49·5	0·7592	0·8231
	Dark	2·3720	1·9010	0·1217	0·1316	21·0	0·7592	0·8202
17. 250 gms. soil + 0·5% carbon as W.S. + 0·5% P_2O_5 as G.B.S. + Anabaena naviculoides	Light	2·3720	1·6890	0·1217	0·1547	48·3	0·7640	0·8358
	Dark	2·3720	1·9010	0·1217	0·1317	21·2	0·7640	0·8248
18. 250 gms. soil + 0·5% carbon as W.S. + 0·5% P_2O_5 as G.B.S. + Tolypothrix tenuis	Light	2·3720	1·6980	0·1217	0·1557	50·5	0·7640	0·8358
	Dark	2·3720	1·9000	0·1217	0·1318	21·4	0·7640	0·8246
19. 250 gms soil + 0·5% carbon as Sunhemp	Light	2·3730	1·6480	0·1655	0·1773	16·0	0·0524	0·0552
	Dark	2·3730	1·9370	0·1655	0·1702	10·8	0·0524	0·0542
20. 250 gms. soil + 0·5% carbon as sunhemp + Anabaena naviculoides	Light	2·3730	1·7670	0·1655	0·1855	33·0	0·0524	0·0554
	Dark	2·3730	1·9528	0·1655	0·1705	11·9	0·0524	0·0544
21. 250 gms. soil + 0·5% carbon as sunhemp + Tolypothrix tenuis	Light	2·3730	1·7650	0·1655	0·1863	33·7	0·0524	0·0558
	Dark	2·3730	1·9563	0·1655	0·1705	12·0	0·0524	0·0544
22. 250 gms. soil + 0·5% carbon as sunhemp+0·5% P_2O_5 as T.B.S.	Light	2·7330	1·1680	0·1655	0·1890	31·1	0·7592	0·8204
	Dark	2·3730	1·8971	0·1655	0·1726	15·0	0·7592	0·8172
23. 250 gms. soil + 0·5% carbon as sunhemp+0·5% P_2O_5 as G.B.S.	Light	2·3730	1·6060	0·1655	0·1912	33·5	0·7640	0·8344
	Dark	2·3730	1·8790	0·1655	0·1735	16·1	0·7640	0·8239
24. 250 gms. soil + 0·5% carbon as sunhemp +0·5% P_2O_5 as T.B.S. + Anabaena naviculoides	Light	2·3730	1·6690	0·1655	0·1965	44·0	0·7592	0·8220
	Dark	2·3730	1·8890	0·1655	0·1749	19·4	0·7592	0·8196
25. 250 gms. soil + 0·5% carbon as sunhemp + 0·5% P_2O_5 as T.B.S. + Tolypothrix tenuis	Light	2·3730	1·6670	0·1655	0·1973	45·0	0·7592	0·8224
	Dark	2·3730	1·8890	0·1655	0·1751	19·8	0·7592	0·8197
26. 250 gms. soil + 0·5% carbon as sunhemp + 0·5% P_2O_5 as G.B.S. + Anabaena naviculoides	Light	2·3730	1·6640	0·1655	0·1974	45·0	0·7640	0·8353
	Dark	2·3730	1·8710	0·1655	0·1754	19·7	0·7640	0·8241
27 250 gms. soil + 0·5% carbon as sunhemp+0·5% P_2O_5 as G.B.S. + Tolypothrix tenuis	Light	2·3730	1·6520	0·1655	0·1990	47·2	0·7640	0·8352
	Dark	2·3730	1·8680	0·1655	0·1755	19·8	0·7640	0·8242

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Effect of Algae and Azotobacter on Carbon Nitrogen Transformations in Gangapur Soil

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Abstract

The amount of nitrogen fixed by Anabaena, Tolypothrix and Azotobacter is small in comparison to the nitrogen fixed by wheat straw, though some saving of carbon is observed in all systems inoculated with algae along with nitrogen fixation exposed to light.

Introduction

The origin of soil nitrogen has been highly controversial. A huge amount of nitrogen is removed from the arable lands every year through various processes such as harvest of crops, erosion, leaching and loss as elementary nitrogen from the surface[1,2]. It is obvious therefore, that in order to maintain their fertility, soil must have some mechanism by which they are able to fix nitrogen from some source and thus make up the loss totally or partially. Various soil scientists have suggested different mechanisms to explain nitrogen fixation in soil.

Barnes[3] from the Woburn Experiment Station has reported an increase in the nitrogen content with straw undergoing oxidation. Bjälfve[4] in Sweden has also observed that straw, when ploughed in fixes atmospheric nitrogen by the slow oxidation of straw in soil.

Soils can also fix nitrogen by some free living nitrogen fixing organisms present in them. De[5] obtained with Aulosira fertilissima fixation amounting to 0·05 mg/100 ml. of nitrogen in 45 days. De and Sulaiman[6] conducted pot epxeriments with rice plants and observed that pots inoculated with algae showed a nitrogen fixation of 30–40 p.p.m, where as in the absence of such algae, nitrogen loss was recorded.

Fritsch and De[7] have concluded that nitrogen fixation in paddy soils is purely through the agencies of algae and that the part played by bacteria is relatively unimportant. On the other hand Uppal, Patel and Daji[8] have shown that Azotobacter plays an important role in the nitrogen recuperation of rice soils in Karjat (India).

Ressell[9] has stated "there is no evidence yet that algae play an important role in enriching the soils of temperate regions with nitrogen although species belonging to the genera containing nitrogen fixing forms are fairly widespread.

From this brief review it can be seen that no definite information is available regarding the amount of nitrogen fixed by blue green algae and azotobacter under ordinary conditions and the subject needs further study. Hence it was thought of interest to study quantitatively the part played by the algae or azotobacter in enriching the soil. Two species of blue green algae, namely Anabaena naviculoides

and Tolypothrix tenuis and one species of green alga Chlorella vulgaris and azotob-acter were inoculated in the soil and the increase in nitrogen determined after definite intervals of time and compared with the increase obtained by mixing the soil with wheat straw at the corresponding intervals.

Experiment

The experiments were carried out with Gangapur Soil. All the ingredient *viz.*, soil, wheat straw used in these experiment were sieved to 100 mesh. 200 gms of soil were taken in 20 cm. enamelled dishes. To this 1% carbon as wheat straw was added on oven dry basis and the contents were thoroughly mixed in a big pestle and mortar and the whole mixture was made as uniform as possible. Then where ever required the soil in the dishes was inoculated with the algae or azotobacter. Sets were arranged in duplicate, one of which was exposed to light under electric bulb and other was covered with thick black cloth. Moisture was maintained at 40% level throughout the experiment. The contents of the dishes were stirred daily with the help of a glass rod. At regular intervals of time, composite samples were taken out from all the dishes and were analysed for total carbon, nitrogen, ammoniacal nitrogen and nitrate nitrogen. Bacteria free unialgal cultures of the above algae were obtained from Dr. A. K. Mitra, an eminent algologist, University of Allahabad. Stock culture of these algae were then prepared by growing them in the following media.

	Medium for Anabaena and Tolypothrix	For Chlorella
KNO_3	0·2	...
NH_4NO_3	...	0·2 gm.
K_2HPO_4	0·2 gm.	0·2 gm.
$MgSO_4$	0·2 gm.	0·2 gm.
$CaCl_2$	0.1 gm.	0·1 gm.
$FeCl_3$ (1%)	2 drops	2 drops
Pyrex distilled water	1000 c.c.	1000 c.c.

Percentage Analysis of Wheat straw and Soil used

	Wheat straw	Soil
Loss on ignition	90·7263	—
Ash	9·082	—
HCl insoluble	5·126	75·1638
Sesquioxide	1·4154	14·264
Fe_2O_3	0·6064	1·1239
Total P_2O_5	0·6038	0·1432
CaO	0·8442	1·046
K_2O	0·8036	0·9862
MgO	0·4078	1·3784
Total Carbon	38·276	0·1515
Total Nitrogen	0·628	0·0278
NH_3–N	—	0·0010
NO_3–N	—	0·0019

[450]

TABLE 1

200 gms. soil   *Av. Temp.* 29°C

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	NH₃—N gm.	NO₃—N gm.	Efficiency N fixed per gm. of C oxidised	pH

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	NH_3—N gm.	NO_3—N gm.	Efficiency N fixed per gm. of C oxidised	pH
Light						
0	0·3030	0·0556	0·0020	0·0038	—	8·25
60	0·2622	0·0560	0·0024	0·0044	9·8	8·10
120	0·2301	0·0563	0·0027	0·0048	9·6	7·95
180	0·1944	0·0566	0·0031	0·0052	9·2	7·90
240	0·1846	0·0567	0·0029	0·0049	—	7·80
Dark						
0	0·3030	0·0556	0·0020	0·0038	—	8·25
60	0·2736	0·0558	0·0023	0·0043	6·8	8·15
120	0·2562	0·0559	0·0026	0 0046	6·4	7·95
180	0·2183	0·0561	0·0030	0·0051	5·9	7·90
240	0·2054	0·0562	0·0028	0·0046	—	7·85

TABLE 2

200 gms soil + Chlorella

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	NH_3—N gm.	NO_3—N gm.	Efficiency N fixed per gm. of C oxidised	pH
Light						
0	0·3030	0·0556	0·0020	0·0038	—	8·25
60	0·2642	0·0563	0·0022	0·0042	18·0	7·90
120	0·2340	0·0567	0·0025	0·0046	15·9	7·70
180	0·1989	0·0571	0·0028	0·0049	14·8	7·45
240	0·1874	0·0573	0·0027	0·0047	—	7·30
Dark						
0	0·3030	0·0556	0·0020	0·0038	—	8·25
60	0·2737	0·05581	0·0023	0·0040	7·1	8·15
120	0·2559	0·05592	0·0024	0·0045	6·7	8·00
180	0·2181	0·05614	0·0029	0·0050	6·4	7·90
240	0·2052	0·05621	0·0028	0·0046	—	7·80

TABLE 3

200 gms. soil + Anabaena

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	NH_3—N gm.	NO_3—N gm.	Efficiency N fixed per gm. of C oxidised	pH
Light						
0	0·3030	0·0556	0·0020	0·0038	—	8·25
60	0·2638	0·0567	0·0024	0·0042	28·0	7·95
120	0·02326	0·0574	0·0036	0·0043	26·8	7·75
180	0·1967	0·0582	0·0029	0·0049	24·7	7·50
240	0·1866	0·0584	0·0030	0·0048	—	7·35
Dark						
0	0·3030	0·0556	0·0020	0·0038	—	8·25
60	0·2736	0·05582	0·0022	0·0040	7·4	8·15
120	0·2561	0·05592	0·0025	0·0044	6·5	8·00
180	0· 182	0·056·5	0·0028	0·0050	6·4	7·90
240	0·2051	0·05622	0·0028	0·0047	—	7·80

TABLE 4

200 gm. soil + Tolypothrix   *Av. Temp. 29°C*

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	NH_3–N gm.	NO_3–N gm.	Efficiency	pH
			Light			
0	0·3030	0·0556	0·0020	0·0038	—	8·25
60	0·2642	0·0568	0·0024	0·0041	30·9	7·95
120	0·2334	0·0576	0·0025	0·0044	28·7	7·75
180	0·1981	0·0584	0·0031	0·0048	26·6	7·50
240	0·1872	0·0586	0·0030	0·0047	—	7·35
			Dark			
0	0·3030	0·0556	0·0020	0·0038	—	8·25
60	0·2737	0·05582	0·0022	0·0040	7·5	8·15
120	0·2562	0·05592	0·0026	0·0043	6·8	8·00
180	0·2182	0·05615	0·0028	0·0046	6·4	7·90
240	0·2052	0·05622	0·0027	0·0048	—	7·80

TABLE 5

200 gm. soil + Azotobacter

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	NH_3–N gm.	NO_3–N gm.	Efficiency	pH
			Light			
0	0·3030	0·0556	0·0020	0·0038	—	8·25
60	0·2617	0·0562	0·0024	0·0043	14·5	8·10
120	0·2288	0·0566	0·0027	0·0047	13·4	7·90
180	0·1932	0·0570	0·0031	0·0050	12·7	7·85
240	0·1834	0·0571	0·0029	0·0049	—	7·75
			Dark			
0	0·3030	0·0556	0·0020	0·0038	—	8·25
60	0·2732	0·05582	0·0022	0·0043	7·3	8·15
120	0·2558	0·05592	0·0027	0·0045	6·7	8·00
180	0·2176	0·05615	0·0030	0·0050	6·4	7·90
240	0·2044	0·05622	0·0027	0·0047	—	7·80

TABLE 6

200 gm. soil + 1% C as wheat straw

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	NH_3–N gm.	NO_3–N gm.	Efficiency	pH
			Light			
0	2·3030	0·0889	0·0020	0·0039	—	8·25
60	1·9350	0·0990	0·0034	0·0058	27·4	7·70
120	1·7295	0·1045	0·0047	0·0079	27·2	0·25
180	1·5549	0·1091	0·0051	0·0086	27·0	7·10
240	1·3478	0·1145	0·0048	0·0082	26·8	6·90
			Dark			
0	2·3030	0·0889	0·0020	0·0038	—	8·25
60	2·0163	0·0930	0·0028	0·0047	14·3	7·75
120	1·8562	0·0952	0·0034	0·0054	14·1	7·40
180	1·6987	0·0973	0·0041	0·0062	13·9	7·15
140	1·5711	0·0990	0·0039	0·0059	13·8	6·95

TABLE 7

200 gms. soil + 1% C as wheat straw + Chlorella   *Av. Temp. 29°C*

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	NH$_3$–N gm.	NO$_3$–N gm.	Efficiency	pH
Light						
0	2·3030	0·0889	0·0020	0·0038	—	8·25
60	2·0185	0·0992	0·0031	0·0056	36·2	7·55
120	1·8629	0·1047	0·0044	0·0076	35·9	7·20
180	1·6837	0·1094	0·0048	0·0083	33·1	7·05
240	1·4968	0·1147	0 0045	0·0076	32·0	6·75
Dark						
0	2·3030	0·0889	0·0020	0·0038	—	8·25
60	2·01633	0·0930	0·0027	0·0046	14·3	7·75
120	1·85626	0·0952	0·0033	0·0053	14·1	7·35
180	1·6987	0·0973	0·0042	0·0061	13·9	7·20
240	1·5711	0·0990	0·0038	0·0058	13·8	6·95

TABLE 8

200 gms. soil + 1% C as wheat straw + Anabaena

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	NH$_3$–N gm.	NO$_3$–N gm.	Efficiency	pH
Light						
0	2·3030	0·0889	0·0020	0·0038	—	8·25
60	2·0148	0·1017	0·0032	0·0054	44·4	7·60
120	1·8607	0·1081	0·0045	0·0073	43·4	7·25
180	1·6832	0·1157	0·0050	0·0082	43·2	7·10
240	1·4962	0·1228	1·0046	0·0078	42·1	6·80
Dark						
0	2·3030	0·0889	0·0020	0·0038	—	8·25
60	2·0163	0·0930	0·0028	0·0047	14·3	7·75
120	1·8562	0·0952	0·0032	0·0054	14·1	7·35
180	1·6987	0·0973	0·0043	0·0061	13·9	7·20
240	1·5711	0·0990	0·0039	0·0059	13·8	6·95

TABLE 9

200 gms. soil + 1% C as wheat straw + Tolypothrix

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	NH$_3$–N gm.	NO$_3$–N gm.	Efficiency	pH
Light						
0	2·3030	0·0889	0·0020	0·0038	—	8·25
60	2·0162	0·1023	0·0032	0·0054	46·7	7·65
120	1·8612	0·1093	0·0046	0·0074	46·3	7·30
180	1·6836	0·1175	0·0051	0·0081	46·2	7·10
240	1·4962	0·1260	0·0047	0·0077	46·0	6·80
Dark						
0	2·3030	0·0889	0·0020	0·0038	—	8·25
60	2·0163	0·0930	0·0028	0·0047	14·3	7·75
120	1·8562	0·0952	0·0032	0·0055	14·1	4·35
180	1·6987	0·0973	0·0042	0·0062	13·9	7·20
240	1·5711	0·0990	0·0038	0·0080	13·8	6·95

TABLE 10

200 gms. soil + 1% C as wheat straw + Azotobacter   *Av. Temp.* 29°C

Period of exposure in days	Total carbon gm.	Total nitrogen gm.	NH_3—N gm.	NO_3—N gm.	Efficiency	pH
			Light			
0	2·3030	0·0889	0·0020	0·0038	–	8·25
60	2·0152	0·0998	0·0033	0·0056	37·8	7·70
120	1·8574	0·1057	0·0046	0·0076	37·7	7·35
180	1·6828	0·1102	0·0050	0·0084	37·4	7·10
240	1·4956	0·1187	0·0047	0·0081	37·0	6·90
			Dark			
0	2·3030	0·0889	0·0020	0·0038	–	8·25
60	2·0093	0·0931	0·0027	0·0045	14·3	7·75
120	1·8523	0·0953	0·0032	0·0052	14·2	7·40
180	1·6943	0·0973	0·0043	0·0059	13·8	7·15
240	1·5604	0·0990	0·0039	0·0058	13·6	6·95

Discussion

A perusal of the experimental results shows that there is a decrease in the carbon content of the system with concomitant increase of nitrogen when wheatstraw is mixed with soil and allowed to undergo slow oxidation in air. It is further observed that the increase in the nitrogen fixed are in following order :

Wheat straw > Tolypothrix > Anabaena > Azotobacter > Chlorella.

It is interesting to note that in the sets inoculated with algae, some saving in carbon and a small increase in nitrogen was always found in light though in the dark there was no significant difference in the carbon and nitrogen of the system. The order of carbon saving was Chlorella > Tolypothrix > Anabaena. This is in agreement with the observation of Williams and Burris[10] and many other workers that the growth rates of blue green algae are much smaller than those for Chlorella. In sets inoculated with Chlorella there is a slightly greater increase in nitrogen than those of uninoculated ones. It is interesting to note that though Chlorella is not a nitrogen fixer, even then it shows a small fixation of nitrogen in light. The probable reason of this seems to be that in soils, Chlorella lives in smbiosis with nitrogen fixing microorganism, azotobactor[11]. During this process it supplies the azotobacter with carbohydrates and the bacteria in turn fixes nitrogen. In the sets inoculated with Tolypothrix and Anabaena, there is appreciable increase in the nitrogen content over that of control sets, the increase being greater in the case of Tolypothrix than in that of Anabaena. This is in agreement with the general observations made by various algologists that Tolypothrix is a better fixer of nitrogen than Anabaena.

From the experimental results it is clear that the efficiency of nitrogen fixation is always found to be greater in sets inoculated with algae and azotobacter than those without it. In sets inoculated with azotobacter there is small increase of nitrogen than the control and sets inoculated with Chlorella more in light than in dark, though the azotobacter number is larger in the sets covered with black cloth than in the system exposed to light. Ziemiecka[12] observed that by the addition of organic matter, the soil population becomes large. Waksman[13] and Miller[14] have also observed that the number of bacteria is smaller on the surface exposed to

sunlight. It is clear from the results that the fixation of nitrogen in systems exposed to light is almost double as compared to the fixation of nitrogen in the corresponding systems covered with black cloth, thereby showing the negligible part played by azotobacter in increasing the nitrogen, whereas in the systems with wheat straw, an appreciable increase in nitrogen is observed. Recently Jensen[15] in Denmark, Stockli[16] in Zurich and Lemoigne[17] in Paris have confirmed the small part played by azotobacter in improving the nitrogen status of the soil.

It is interesting to rocord that with Anabaena and Tolypothrix the efficiency is always found to be greater than that of Chlorella and azotobacter. This is because along with carbon saving, both Anabaena and Tolypothrix being nitrogen fixers are able to increase the nitrogen content of the system thus giving higher efficiency. It is observed there is an increase in the available nitrogen more in the exposed sets than in the covered sets. A decrease in the available nitrogen of the system is observed in all the sets inoculated with algae than that in the uninoculated ones. This indicates that some of the available nitrogen of the soil is utilized by the algae during the growth for building the algal cell.

A decease in pH is observed in systems containing organic matter. The sets inoculated with algae also show a slight decrease in pH. The decrease in pH is more in the exposed sets than in the covered ones. During the slow oxidation of organic matter organic acids are produced and finally the carbonic acid which decreases the pH of the system.

Thus it is concluded that small amounts of nitrogen are fixed by Anabaena, Tolypothrix and azotobacter. Some saving of carbon is observed in all the systems inoculated with algae along with nitrogen fixation when exposed to light. The contribution of algae and azotobacter in increasing the nitrogen status of soil is very small as compared to that of organic matter.

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Solubility of some Rock Phosphates and Basic Slags in Sodium Bicarbonate, Sodium Carbonate and Sodium Hydroxide Solutions

By

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Abstract

It has been observed that the P_2O_5 solubility of Tata, German and Belgian basic slags and Trichinopoly, Bihar and Algerian rock phosphates is maximum in sodium hydroxide solution, followed by sodium carbonate and minimum in sodium bicarbonate, whilst the solubility of Kulti and Durgapur basic slags is highest in sodium bicarbonate solution and lowest in sodium hydroxide solution. It is evident from the results that from alkali solubilization point of view Tata, German and Belgian basic slags are decidedly better source of phosphatic fertilizers than Trichinopoly, Bihar and Algerian rock phosphates.

Introduction

The value of phosphate fertilizers as sources of phosphorus for plants depends upon many soil properties and the availability of phosphorus in the products fomed as a result of the reaction between the fertilizers and soils[1-3]. According to Dos Santos *et al*[4] the availability is a general property of the soil plant system and not of soil alone. Phosphorus occurs in the soil in different forms and compounds, but all of them are not equally available to the plants. Inorganic phosphates in the soils can be classified to four forms, *i.e.*, calcium phosphate, iron phosphate, aluminium phosphate and reductant soluble phosphates. Russell[5], Dean[6] and Ghani and Aleem[7] have worked on this subject. According to Chirikov and Volkova[8], the least available form is the alkali soluble fraction. The conventional methods for the determination of available phosphorus appear to extract a portion of all chemical forms and the availability of the respective phosphorus fractions, however, is difficult to ascertain.

As plants can utilize different forms of soluble phosphates, several extraction methods to determine the availability of phosphate in soils have been recommended. Among the alkali extraction methods the use of sodium bicarbonate solution has been proposed, the theory being HCO_3^- ion reduces activity of the Ca^{++} ion in calcareous soils and thereby increases the solubility of phosphorus[9]. Jones[10] has recommended the use of 0·5 N sodium hydroxide solution but Saunder[11] proposed the use of 0·1 N sodium hydroxide solution for the determination of available phosphate.

In view of the above an attempt has been made by the authors to determine the solubility of Tata, Kulti, Durgapur, German and Belgian basic slags and Trichinopoly, Bihar and Algerian rock phosphates in sodium carbonate, sodium bicarbonate and sodium hydroxide solutions.

Experimental

Sample : The composition of all the naturally occurring rock phosphates and basic slags (except Durgapur basic slag) utilised in these experiments is the same as described in the paper[12] dealing with the influence of temperature on the hydrolysis of these materials. Durgapur basic slag contains $20 \cdot 16\%$ SiO_2, $3 \cdot 48\%$ P_2O_5, $6 \cdot 87\%$ Al_2O_3, $12 \cdot 18\%$ Fe_2O_3, $37 \cdot 77\%$ CaO and $5 \cdot 67\%$ MgO.

Solubility determination : $1 \cdot 00$ gm of rock phosphates or basic slags sieved through a 200 mesh sieve was taken in Jena Glass bottles and 100 ml of alkali solution was added to it. It was shaken in a mechanical shaker for one hour and then placed in a thermostat maintained at a temperature at 30°C. After 24 hours it was filtered and aliquot portions of the filtrate were utilised for the determination of P_2O_5[13,14].

Results

TABLE 1

Material	0·1 N NaHCO$_3$	0·1 N Na$_2$CO$_3$	0·1 N NaOH	0 2 N NaOH
Tata basic slag	0·3413	0·3807	0·4895	0·5877
Kulti basic slag	0·2149	0·1497	0·0972	0·1025
German basic slag	0·6091	0·6355	0·7398	0·8900
Belgian basic slag	0·5398	0·5844	0·7275	0·8737
Durgapur basic slag	0·2041	0·1352	0·0902	0·0998
Trichinopoly rock phosphate	0·1705	0·1773	0·2529	0·2982
Bihar rock phosphate	0·1681	0·1891	0·2369	9·2709
Algerian rock phosphate	0·2078	0·2390	0·2605	0·3307

Discussion

The results obtained by treating Tata, Kulti, German, Belgian and Durgapur basic slags and Trichinopoly, Bihar and Algerian rock phosphates with the solutions of sodium hydroxide, sodium carbonate and sodium bicarbonate have been recorded in Table 1. It has been observed that except for Kulti and Durgapur basic slags their general behaviour shows the same trend as other phosphates[15]. The solubility of Kulti and Durgapur basic slags is highest in sodium bicarbonate solution and lowest in sodium hydroxide solution, whilst, the solubility of other substances is highest in sodium hydroxide solution followed by sodium carbonate and least in sodium bicarbonate. It appears that complex silicophosphates in Kulti and Durgapur basic slags are more suseptible by milder alkalies like sodium bicarbonate and sodium carbonate than sodium hydroxide. When sodium carbonate or sodium bicarbonate is added to Tata, German and Belgian basic slags, a part of iron and aluminium phosphates present in them is converted into sodium phosphates with the liberation of iron and aluminium hydroxides. But these two mildly alkaline reagents when added to Kulti and Durgapur basic slags containing more silicates than phosphates can readily precipitate carbonates of calcium and magnesium with the formation of sodium phosphates in soluble condition. This may explain the behaviour of sodium bicarbonate in producing greater amounts of P_2O_5 than that obtained by sodium hydroxide. According to Kroll[16] silico-carnotite 3 CaO. P_2O_5 : 2 CaO, Hilgenstockite 4 CaO.P_2O_5 Steadite 3 ($CaO.P_2O_5$) : 2 CaO : 2 CaO.SiO_2 and

Thomasite 6 $CaO.P_2O_5 : 2 FeO.SiO_2$, occur in basic slags. It seems that Thomasite is likely to be present in greater amounts in the phosphate rich basic slags because phosphate of iron present in Thomasite can be broken up into ferric and ferrous hydroxides and Sodium phosphates. On the other hand Silico–carnotite, Hilgenstockite and steadite not containing ferrous and f rric compounds cannot produce sodium phosphates as much as Thomasite by the action of sodium hydroxide. It appears that Hilgenstockite, silico–carnotite and steadite are likely to be present in larger amounts than Thomasite in Kulti and Durgrpur basic slags. Thus by adding sodium carbonate or sodium bicarbonate solution to the suspensions of Silico–carnotite, Hilgenstockite and Steadite, calcium carbonate is likely to be precipitated and a part of the sparingly soluble phosphate is converted into sodium phosphates. Hence, by treating with sodium carbonate and sodium bicarbonate solutions, more P_2O_5 comes out in the solutions with Kulti and Durgapur basic slags than by treating with sodium hydroxide solutions. The increase in the solubility of rock phosphates is due to the decomposition of calcium phosphates present in them to more soluble sodium phosphates.

These results, therefore, establish that from alkali solubilization point of view Tata, German and Belgian basic slags are decidedly better source of phosphatic fertilizers than Trichinopoly, Bihar and Algerian rock phosphates and Kulti and Durgapur basic slags.

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Effect of different Composts on the yield of Barley Grain and Barley Straw, Paddy Grain and Paddy Straw in Pots

By

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Introduction

We have studied the effect of different composts like phosphated municipal rubbish, leaf compost and unphosphated municipal rubbish prepared by us on the yield of barley grain grown in the month of November, 1960 and paddy grown in the month of July, 1961 in the same pots without further treatments.

Methods and Materials

For pot experiments the soil was collected from Sheila Dhar Institute's garden. It was dried, well powdered and thoroughly mixed. 10 lbs of this soil was filled up in each earthen pot. In these earthen pots, well decomposed leaf compost, phosphated and unphosphated municipal rubbish composts were properly mixed and added at the rate of 10 tons/acre and 5 tons/acre. Replication was carried out six times for each treatment. After making it unifrom, 8 seeds of barley grain were sown in each earthen pot and they were covered with a wire net to avoid birds and other harmful insects, and, a proper care was taken.

After an interval of 15 days, sufficient amount of water was added to maintain the suitable moisture for barley crop.

The following treatments were undertaken :

1.	Phosphated municipal rubbish	5 tons/acre
2.	,, ,,	10 tons/acre
3.	Leaf compost	5 tons/acre
4.	,, ,,	10 tons/acre
5.	Unphosphated municipal rubbish	6 tons/ acre
6.	,, ,,	10 tons/acre
7.	Soil alone (control)	

Date of sowing	4–11–60
Date of harvesting	22–3–61
Number of seeds in each pot	8
,, ,, treatments	7
,, ,, replication	6
Total number of earthen pots	42

TABLE 1
Analysis of materials used

	Leaf compost %	Phosphated municipal rubbish %	Unphosphated municipal rubbish %	Soil %
Loss on ignition	21·9100	6·2400	10·6500	4·2600
Ash	78·0900	93·7600	89·3500	95·7400
HCl insoluble	62·8594	77·9319	75·3200	85·6738
Sesquioxide	9·2800	10·2300	10·0600	7·9600
Fe_2O_3	3·8700	3·6600	4·7200	2·0900
P_2O_5	0·9216	1·2156	0·8525	0·3672
Available P_2O_5 (1% citric acid solution)	0·2857	0·2650	0·2453	0·0527
CaO	2·6542	3·2162	1·8425	0·8634
MgO	0·2852	0·2615	0·2506	0·1665
K_2O	1·8622	0·8054	0·7521	0·5727
Total Carbon	8·6900	4·1600	6·2700	0·4146
Total Nitrogen	2·4500	1·2500	0·8242	0·0421
$NH_3 - N$	0·0754	0·0542	0·0268	0·0009
$NO_3 - N$	0·1449	0·1145	0·0506	0·0016
Total available N over Total N	15·2	13·5	9·4	6·1
C/ Ratio	5·9	3·3	7·6	10·2

TABLE 2
Composition of soil after mixing different composts
Treatments

	10 lbs soil + 52 gms Phosphated M.R.	10 lbs soil + 26 gms Phosphated M.R.	10 lbs soil + 52 gms leaf composts	10 lbs soil + 26 gms leaf composts	10 lbs soil + 52 gms unphosphated M.R.	10 lbs soil + 26 gms unphosphated M.R.	Soil alone (control)
Sesquioxide %	7·974	7·916	7·964	7·911	7·973	7·915	4·960
Iron oxide %	2·108	2·084	2·110	2·089	2·121	2·092	2·090
Total P_2O_5 %	0·3786	0·3611	0·3735	0·3682	0·3727	0·3678	0·3602
Available P_2O_5 (1% citric acid solution) %	0·0562	0·0541	0·0553	0·0537	0·0544	0·0534	0·0527
Total CaO %	0·8901	0·8718	0·8857	0·8686	0·8745	0·8640	0·8634
Total K_2O %	0·5753	0·5708	0·5873	0·5767	0·5747	0·5704	0·5727
Total MgO %	0·1675	0·1660	0·1678	0·1662	0·1674	0·1660	0·1665
Total Carbon %	0·4670	0·4335	0·5085	0·4493	0·4811	0·4455	0·4146
Total Nitrogen %	0·0559	0·0489	0·0581	0·0499	0·0510	0·0436	0·0421
$NH_3 - N$ %	0·0015	0·0011	0·0017	0·0013	0·0013	0·0011	0·0009
$NO_3 - N$ %	0·0029	0·0022	0·0032	0·0024	0·0022	0·0019	0·0016
Total available N %	0·0044	0·0033	0·0049	0·0037	0·0035	0·0020	0·0025
C/N ratio	8·3	0·8	8·7	9·2	9·4	9·6	10·2

TABLE 3

Analysis of soil after the harvesting of Barley

Treatments

	10 lbs soil +52 gms phosphated M.R.	10 lbs soil +26 gms phosphated M.R.	10 lbs soil +52 gms leaf compost	10 lbs soil +26 gms leaf compost	10 lbs soil +52 gms unphosphated M.R.	10 lbs soil +26 gms unphosphated M.R.	Soil alone (control)
Sesquioxide %	7·968	7·902	7·950	7·906	7·967	7·912	7·923
Iron oxide %	2·097	2·071	2·093	2·081	2·118	2·081	2·042
Total P_2O_5 %	0·3754	0·3610	0·3720	0·3672	0·3720	0·3668	0·3660
Available P_2O_5 1 % citric acid solution) %	0·0543	0·0520	0·0536	0·0522	0·0530	0·0525	0·0512
Total CaO %	0·8890	0·8715	0·8830	0·8675	0·8742	0·8639	0·8653
Total K_2O %	0·5745	0·5696	0·5866	0·5754	0·5735	0·5661	9·5720
Total MgO %	0·1668	0·1651	0·1671	0·1653	0·1662	0·1660	0·1663
Total carbon %	0·4220	0·4096	0·4620	0·4332	0·4356	0·4232	0·4065
Total Nitrogen %	0·0543	0·0465	0·0563	0·0478	0·0512	0·0445	0·0418
NH_3 – N %	0·0016	0·0012	0·0013	0·0013	0·0012	0·0013	0·0010
NO_3 – N %	0·0027	0·0019	0·0027	0·0023	0·0021	0·0018	0·0015
Total available N %	0·0043	0·0041	0·0040	0·0036	0·0033	0·0031	0·0025
C/N ratio	7·6	8·6	8·2	9·0	8·4	9·5	9·7

TABLE 4

Yield of Barley grain in Pots from different composts (gms)

Replication

Treatments	1	2	3	4	5	6	Total
Phosphated M. R. (5 tons/acre)	33	28	33	29	30	28	181
Phosphated M. R. (10 tons/acre)	42	40	39	43	45	44	253
Leaf compost (5 tons/acre)	28	26	29	24	26	25	158
Leaf compost (10 tons/acre)	40	38	39	36	42	41	226
Unphosphated M. R. (5 tons/acre)	22	24	25	21	18	23	133
Uhphosphated M. R. (10 tons/acre)	31	35	30	34	32	31	193
Soil alone (control)	9	8	7	6	12	8	50
Total	205	199	202	193	205	200	1194

TABLE 5
Analysis of variance for the yield of Barley grains

Due to	D. F.	S. S.	M. S.	Calculated F	F from table 1%	F from table 5%	Level of significance
Total	41	5366·3	130·88	–	–	–	Yield is
Treatments	6	4430·9	738·48	63·66	2·42	3·47	highly
Replications	5	585·4	117·0	10·00	2·53	3·70	significant.
Error	30	350·0	11·6	–	–	–	

TABLE 6
Yield of Barley straw in Pots from different composts (gms)

Treatments	Replications 1	2	3	4	5	6	Total
Phosphated M. R. (5 tons/acre)	44	46	45	43	45	47	270
Phosphated M. R. (10 tons/acre)	63	65	67	70	68	66	399
Leaf compost (5 tons/acre)	39	42	38	43	40	41	243
Leaf compost (10 tons/acre)	58	60	62	63	63	59	365
Unphosphated M. R. (5 tons/acre)	32	35	34	33	36	35	205
Unphosphated M. R. (10 tons/acre)	53	54	48	52	51	49	307
Soil alone (control)	17	16	21	20	22	18	114
Total	306	318	315	324	325	315	1903

TABLE 7
Analysis of variance for the yield of Barley straw

Due to	D. F.	S. S.	M. S.	Calculated F	F from the table 1%	F from the table 5%	Level of significance
Total	41	9529·0	232·4	–	–	–	Yield is
Treatments	6	9382·5	1563·2	489·9	2·42	3·47	highly
Replications	5	41·1	9·8	3·0	2·53	3·70	significan
Error	30	97·4	3·2	–	–	–	

TABLE 8
Yield of Paddy grains in Pots from different compost (gms)

Treatments	Replications 1	2	3	4	5	6	Total
Phosphated M. R. (5 tons/acre)	42	40	45	38	41	43	249
Phosphated M. R. (10 tons/acre)	52	55	53	50	52	55	317
Leaf compost (5 tons/acre)	37	35	38	34	36	39	219
Leaf compost (10 tons/acre)	47	49	48	44	45	46	279
Unphosphated M. R. (5 tons/acre)	32	30	34	33	30	31	190
Unphosphated M. R. (10 tons/acre)	41	43	44	42	43	44	257
Soil alone (control)	17	20	18	16	19	18	108
Total	268	276	280	257	266	276	1619

TABLE 9
Analysis of variance for the yield of Paddy grains

Due to	D. F.	S. S.	M. S.	Calculated F	F from table 1%	F from table 5%	Level of significance
Total	41	4723·0	115·1	—	—	—	Yield is
Treatments	6	4610·6	768·4	365·9	2·42	3·47	highly
Replications	5	47·5	9·5	4·5	2·53	3·70	significant
Error	30	64·9	2·1	—	—	—	

TABLE 10
Yield of Paddy straw in Pots from different composts (gms)
Replications

Treatments	1	2	2	4	5	6	Total
Phosphated M. R. (5 tons/acre)	55	54	57	54	58	54	332
Phosphated M. R. (10 tons/acre)	72	76	77	79	78	76	456
Leaf compost (5 tons/acre)	50	50	49	52	53	55	309
Leaf compost (10 tons/acre)	65	68	70	68	69	69	409
Unphosphated M. R. (5 tons/acre)	44	43	45	41	46	45	267
Unphosphated M. R. (10 tons/acre)	55	54	56	55	57	56	330
Soil alone (control)	25	24	27	26	28	23	153
Total	366	369	389	376	389	378	2259

TABLE 11
Analysis of variance for the yield of Paddy straw

Due to	D. F.	S. S.	M. S.	Calculated F	F from table 1%	F from table 5%	Level of significance
Total	41	9691·1	236·3	—	—	—	Yield is
Treatments	6	9084·1	1514·0	76·0	2·42	3·47	highly
Replications	5	48·5	9·7	0·4	2·53	3·70	significant
Error	30	597·4	19·9	—	—	—	

Discussion

From the foregoing results, it is clear that by the addition of different composts like phosphated municipal waste compost, leaf compost and unphosphated municipal waste compost and also at different rates, that is, 5 tons/acre, and 10 tons/acre, to the soil in pots, much better results are obtained than in the control. A good amount of increase of yield in grain and straw was obtained in

the case of barley and paddy crops. The effect of different composts on the yield of grain and straw was in the following order :

Phosphated municipal rubbish > Leaf compost >
Unphosphated municipal rubbish

Acharya and Walunjkai[1] carried out pot experiments on a neutral sandy loam soil from Delhi, growing *Marus* (Eleucine coracana) and Berseem (Trifolium alexandrinum) and found that a mixture of cattle excreta and superphosphate, fermented for a period of 4 months, gave a higher crop yield than the application of an equal amount of compost fermented separately. Struthers and Sieling[2] have shown better crop response by the application of organic manure and phosphate than with the application of phosphate alone to the soil.

Several other workers have reported that the addition of humified organic matter like farm yard manure or compost along with superphosphate helps to minimise the fixation of phosphate in insoluble forms in the soil. Copeland and Muckle[3], Das[4], Aslander[5], Ranjan[6] reported the beneficial effect of compost and phosphate.

Our experiments also prove the same thing because both the composts that is, phosphated municipal rubbish and leaf compost have been prepared through the incorporation of phosphate and have given higher yields in comparison to the unphosphated municipal rubbish. The difference between the yields of these two phosphated composts may be due to the presence of higher amount of phosphate in the phosphated municipal rubbish.

In our experiments beneficial results have also been obtained when the composts are added at the rate of 10 tons/acre than at 5 tons/acre. In the case of 5 tons/acre also the effectiveness of the different composts on the yield is in the same order as in the case of 10 tons/acre.

From our pot experiments we have come to the conclusion that incorporation of phosphated compost is better than the unphosphated compost for the yield of grain and straw for both barley and paddy.

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Influence of Phosphates in Nitrogen Transformations in the Composting of Kans

By

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Introduction

The utilization of decomposing organic matter as a manure was known from anci nt times. The Romans valued the use of decayed materials and prepared manure heaps on their farms. Even in modern times the superior value of farm yard manure has been demonstrated by long and careful experimentation at the Rothamsted Experiment Station.

Russell[1] has reported that the yield of Barley and straw with farmyard manure in Rothamsted field experiments from 1844 till today is better than that obtained with complete artificial fertilizers containing ammonium salts, Potassium salts and phosphate. This is due to the fact that there is more nitrogen in the field manured with farm yard manure than with artificials.

Dhar, in his Presidential Address to the National Academy of Sciences, India, 1952, has stated as follows :

"From our composting experiments we are convinced that calcium phosphate is helpful in the composting of plant materials, specially in the absence of nitrogenous fertilizers because phosphates help in nitrogen fixation by organic matter and, hence, calcium phosphate or phosphate rock should be largely used in composting.

Dswrzbicki[2] stated that phosphate increases nitrogen fixation due to their effect on the metabolism of Azotobacter cells. Lipman[3] observed a similar relationship between phosphorus and nitrogen fixation in the presence of an excess of available energy material.

The importance of phosphorus in Agriculture will be clear by the statement made by Collings[4] :

"Low crop yields are more often due to lack of phosphoric acid than to the lack of any other nutrient. Phosphoric acid has often being called 'the master key' to Agriculture. Phosphoric acid appears to be concerned with the production of nucleoprotieds and it appears that phosphoric acid influences the production of seeds or grain more particularly than does nitrogen or potash."

It has been observed that the availability of mineral phosphates can be increased by composting it with organic matter. Most of the earlier workers, Brown and Warner[5], Lipman and Mclean[6], Hutchinson[7] have shown that ground Phosphate rocks can be converted in part to a more available form by composting it with sulphur and sulphur oxidizing bacteria. In such a compost the sulphur oxidizing organisms convert the sulphur to sulphuric acid, which in turn, act upon phosphate rock and converts a part of it into an available form.

Many investigators[8,9] observed that the organic matter increased the availability of soil phosphate and of rock phosphate which are added to the soil as fertilizer.

[465]

Dhar[10] has observed that when tricalcium phosphate is boiled with distilled water, an appreciable amount of phosphoric acid is dissolved due to hydrolysis according to the following equations :

(1) $Ca_3(PO_4)_2 + 2H_2O = 2CaHPO_4 + Ca(OH)_2$
(2) $Ca_3(PO_4)_2 + 4H_2O = Ca(H_2PO_4)_2 + 2Ca(OH)_2$
(3) $Ca_3(PO_4)_2 + 6H_2O = 2H_3PO_4 + 3Ca(OH)_2$
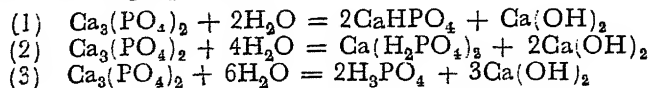
In the soil such hydrolysis of calcium phosphate takes place slowly and phosphates are made available to the crops.

As the function of phosphates in composting is not known, the present investigations were undertaken to determine the influence of different phosphates in the composting of different organic substances. The influence of phosphates was studied on the changes of carbon, nitrogen and C/N ratio of the compost. The effect of decomposting organic matter on the increased availability of added phosphates and the availability of nitrogen in the phosphate treated and the unphosphated composts was also studied. The experiments were carried out in buckets.

Experimental

KANS (Sacchram Spontaneum) obtained was well dried, choff d, and powdered by an electric grinder. A weighed amount of the powdered KANS was placed in buckets and was supplied with a dose of 0·5% P_2O_5 from different sources of phosphatic materials in different buckets.

The reacting mass was mixed well by a glass rod and was kept at a moisture level of 40% throughout the period of the experiment. To facilitate decompostion, the whole mass of each bucket was stirred well thrice per week and the temperature was recorded daily at noon. One set was exposed to the light of 100 W. electric bulb and a corresponding set was kept covered with a thick piece of black cloth.

After a definite interval of time, a portion of the mixture was taken out of each bucket, was oven dried, powdered and sieved and then analysed for total carbon, total nitrogen, ammoniacal nitrogen, nitric nitrogen, and available P_2O_5 etc.

TABLE 2

1 *Kgm Kans* + 40% *moisture (control)*   *At Temp.* 28°C

Period of exposure in days	Total carbon (gms)	Total nitrogen (gms)	NH₃—N (gm)	NO₃—N (gm)	Nitrogen increase (+) or decrease (−) (gms)	Available P_2O_5 %	C/N ratio
			Light				
0	396·4620	6·8170	...	...	...	...	58·1
30	322·5236	8·7450	0·2841	0·3541	+1·9260	0·0362	36·8
60	274·2633	10·5620	0·5625	0·6726	+3·7450	0·0428	25·9
90	254·9251	11·6410	0·6524	1·0355	+4·8240	0·0684	21·8
120	237·0843	11·3290	0·5386	0·8662	+0·3120	0·0724	20·9
			Dark				
0	396·4620	6·8170	...	...	...	...	58·1
30	343·1098	7·9630	0·1982	0·2318	+1·1400	0·0247	43·0
60	312·0156	9·0240	0·2934	0·3924	+2·2070	0·0307	34·5
90	282·6774	10·4020	0·3758	0·6124	+3·5850	0·0418	27·1
120	272·0084	10·2890	0·3075	0·5669	−0·2130	0·0498	26·4

TABLE 3

1 *Kgm Kans* + 0·5% P_2O_5 *as A.R.P.* (A) + 40% *moisture*   *At Temp.* 28°C

Period of exposure in days	Total carbon (gms)	Total nitrogen (gms)	NH_3-N (gm)	NO_3-N (gm)	Nitrogen increase (+) or decrease (−) (gms)	Available P_2O_5 %	C/N ratio
			Light				
0	396·4620	6·8170	..	...	...	...	58·1
30	294·9678	9·7580	0·3043	0·4200	+2·9210	0·0708	30·2
60	254·2206	12·7720	0·5463	0·7820	+5·9550	0·0762	19·9
90	175·9527	14·6230	0·8559	1·3834	+7·8060	0·0849	12·0
120	148·6733	14·1280	0·7534	1·1539	−0·4950	0·0893	10·5
			Dark				
0	396·4620	6·8170	...	...	...	...	58·1
30	320·7378	8·1910	0·2046	0·2623	+1·3740	0·0573	39·1
60	275·5411	10·5240	0·3725	0·4589	+3·7070	0·0625	26·1
90	233·7030	11·8750	0·5075	0·7512	+5·0580	0·0697	19·6
120	187·9230	11·4350	0·4085	0·5634	−0·4400	0 0805	16·4

TABLE 4

1 *Kgm Kans* + 0·5% P_2O_5 *as A.R.P.* (B) + 40% *moisture*

Period of exposure in days	Total carbon (gms)	Total nitrogen (gms)	NH_3-N (gm)	NO_3-N (gm)	Nitrogen increase (+) or decrease (−) (gms)	Available P_2O_5 %	C/N ratio
			Light				
0	396·4620	6·8170	...	...	...	...	58·1
30	300·1218	10·0910	0·3045	0·4826	+3·2740	0·0735	29·7
60	236·5879	12·4960	0·5325	0·7546	+5·6790	0·0795	18·8
90	189·7160	15·0270	0·8374	1·5367	+8·2100	0·0876	12·5
120	151·4485	14·3560	0·6528	1·2709	−0·6710	0·0895	10·5
			Dark				
0	396·4620	6·8170	...	...	...	...	58·1
30	327·0812	8·6480	0·2185	0·2485	+1·8310	0·0536	37·8
60	272·3694	10·0750	0·3379	0·4883	+3·2580	0·0598	27·0
90	228·3622	12·3270	0·5637	0·8139	+5·5100	0·0642	18·5
120	183·1655	11·9450	0·4326	0·7261	−0·3820	0·0703	15·3

TABLE 5

1 *Kgm Kans* + 0·5% P_2O_5 *as A.R.P.* (C) + 40% *moisture*

Period of exposure in days	Total carbon (gms)	Total nitrogen (gms)	NH_3-N (gm)	NO_3-N (gm)	Nitrogen increase (+) or decrease (−) (gms)	Available P_2O_5 %	C/N ratio
			Light				
0	396·4620	6·8170	...	...	...	...	58·1
30	293·4350	10·3970	0·3285	0·5032	+3·5800	0·0775	28·2
60	224·3975	12·7520	0·5768	0·8769	+5·9350	0·0892	17·5
90	168·8927	15·5630	0·8473	1·6739	+8·7460	0·0972	10·8
120	137·5724	15·0050	0·6528	1·3229	−0·5680	0·0992	9·1
			Dark				
0	396·4620	6·8170	...	..	...	...	58·1
30	315·5838	8·8390	0·2305	0·2733	+2·0220	0·0583	35·7
60	264·0437	10·0750	0·3752	0·4812	+3·2580	0·0614	26·2
90	212·9001	12·7520	0·5739	0·8926	+5·9350	0·0736	16·6
120	172·8575	12·2640	0·4836	0·7532	−0·5060	0·0787	14·1

TABLE 6

1 *Kgm Kans* + 0·5% P_2O_5 *as T.B.S.* + 40% *moisture*   *At Temp.* 28°C

Period of exposure in days	Total carbon (gms)	Total nitrogen (gms)	NH$_3$—N (gm)	NO$_3$—N (gm)	Nitrogen increase (+) or decrease (−) (gms)	Available P$_5$O$_2$ %	C/N ratio
Light							
0	396·4620	6·8170	...	...	..	...	58·1
30	276·3341	10·5870	0·4726	0·5543	+3·7700	0·0827	26·1
60	202·9886	13·2450	0·6535	1·0419	+6·4280	0·0947	15·3
90	145·1051	16·4730	1·2431	1·8374	+9·6560	0·1375	8·8
120	109·0271	15·5380	0·8375	1·7418	−0·9350	0·1403	7·0
Dark							
0	396·4620	6·8170	...	...	...	...	58·1
30	306·4024	9·0470	0·2408	0·3382	+2·2300	0·0603	33·9
60	292·9428	11·2080	0·3629	0·5674	+4·3040	0·0721	22·5
90	183·7513	13·4350	0·6835	0·9959	+6·6180	0·0863	13·7
120	161·3591	12·8530	0·5837	0·7059	−0·5820	0·0912	12·5

TABLE 7

1 *Kgm Kans* + 0·5% P_2O_5 *as K.B.S.* + 40% *moisture*

Period of exposure in days	Total carbon (gms)	Total nitrogen (gms)	NH$_3$—N (gm)	NO$_3$—N (gm)	Nitrogen increase (+) or decrease (−) (gms)	Available P$_5$O$_2$ %	C/N ratio
Light							
0	396·4620	6·8170	...	...	..	...	58·1
30	291·7961	10·2590	0·3406	0·4905	+3·4420	0·0785	28·3
60	217·6577	12·6960	0·5306	0·8913	+5·8790	0·0845	17·1
90	153·4308	16·0580	0·9024	1·7311	+9·2410	0·0987	9·5
120	116·1634	15·3250	0·7346	1·5569	−0·7830	0·1128	7·5
Dark							
0	396·4620	6·8170	...	...	...	...	58·1
30	318·9626	8·5320	0·2125	0·2824	+1·7150	0·0578	36·2
60	256·5110	10·4750	0·3624	0·4547	+3·6580	0·0716	24·4
90	194·8877	13·2180	0·6246	0·8823	+6·4010	0·0836	14·7
120	168·9282	12·5720	0·4758	0·6818	−0·6460	0·0869	13·4

TABLE 8

1 *Kgm Kans* + 0·5% P_2O_5 *as B.R.P.* + 40% *moisture*

Period of exposure in days	Total carbon (gms)	Total nitrogen (gms)	NH$_3$—N (gm)	NO$_3$—N (gm)	Nitrogen increase (+) or decrease (−) (gms)	Available P$_5$O$_2$ %	C/N ratio
Light							
0	396·4620	6·8170	...	...	...	...	58·1
30	303·6899	9·3980	0·3026	0·4116	+2·5810	0·0685	32·3
60	248·1942	11·2210	0·4836	0·6609	+4·4040	0·0743	22·1
90	176·5620	14·1150	0·7329	1·4549	+7·2980	0·0865	12·4
120	156·9920	13·4770	0·6284	1·1506	−0·6380	0·0907	11·6
Dark							
0	396·4620	6·8170	...	...	...	.	58·1
30	331·0758	8·0870	0·2004	0·2525	+1·2770	0·0564	40·9
60	277·5234	9·1730	0·2875	0·4188	+2·3560	0·0598	30·9
90	233·9126	11·5130	0·4372	0·8062	+4·6960	0·0678	20·0
120	195·4558	10·9530	0·3437	0·6192	−0·5600	0·0708	17·8

TABLE 9

1 *Kgm Kans* + 0·5% P_2O_5 *as T.B.P.* + 40% *moisture   At Temp.* 28°C

Period of exposure in days	Total carbon (gms)	Total nitrogen (gm)	NH$_3$—N (gm)	NO$_3$—N (gm)	Nitrogen increase (+) or decrease (−) (gms)	Available P$_2$O$_5$ %	C/N ratio
Light							
0	396·4620	6·8170		...	...		58·1
30	297·3465	9·8890	0·2847	0·4669	+3·0720	0·0746	30·6
60	231·9320	12·7320	0·5463	0·8924	+5·9150	0·0824	18·2
90	172·4620	15·2690	0·8435	1·5232	+8·4520	0·0984	11·2
120	155·9865	14·5290	0·6335	1·3715	−0·7400	0·1023	9·3
Dark							
0	396·4620	6·8170	..	...	...	...	58·1
30	333·0281	8·8230	0·2142	0·2711	+2·0060	0·0597	37·7
60	267·6121	9·9870	0·3625	0·4964	+3·1700	0·0635	26·7
90	223·2082	12·5640	0·5627	0·7942	+6·7440	0·0704	17·7
120	173·8584	11·9380	0·4254	0·8968	−0·6220	0·0768	14·5

TABLE 10

1 *Kgm Kans* + 0·5% P_2O_5 *as super phosphate* + 40% *moisture*

Period of exposure in days	Total carbon (gms)	Total nitrogen (gm)	NH$_3$—N (gm)	NO$_3$—N (gm)	Nitrogen increase (+) or decrease (−) (gms)	Available P$_2$O$_5$ %	C/N ratio
Light							
0	396·4620	6·8170	...	...	...	...	58·1
30	293·3819	9·7350	0·3265	0·4718	+2·9180	0·0758	30·1
60	228·7486	12·7290	0·5623	0·8761	+5·9120	0·0845	17·9
90	178·4080	15·0750	0·7954	1·6468	+8·2380	0·0978	11·7
120	153·5193	14·3820	0·6295	1·4990	−0·6930	0·1124	10·6
Dark							
0	396·4620	6·8170		...	...	...	58·1
30	323·9195	8·3560	0·2136	0·2794	+1·5390	0·0554	30·7
60	269·5942	10·0970	0·3583	0·4798	+3·2800	0·0608	26·6
90	220·8294	12·3450	0·3432	0·8518	+5·5280	0·0735	17·8
120	177·6150	11·5760	0·4836	0·6277	−0·7690	0·0764	15·2

TABLE 11

1 *Kgm Kans* + 0·5% P_2O_5 *as B.B.S.* + 40% *moisture*

Period of exposure in days	Total carbon (gms)	Total nitrogen (gm)	NH$_3$—N (gm)	NO$_3$—N (gm)	Nitrogen increase (+) or decrease (−) (gms)	Available P$_2$O$_5$ %	C/N ratio
Light							
0	396·4620	6·8170	...	..	...	...	58·1
30	271·9730	10·5380	0·4085	0·6137	+3·7210	0·0859	25·8
60	199·4204	13·7620	0·7532	1·0496	+6·9430	0·0983	14·4
90	138·9688	16·8540	1·3081	2·0121	+10·0370	0·1408	8·2
120	104·2696	15·7350	0·9354	1·8182	−1·1190	0·1457	6·6
Dark							
0	396·4620	6·8170	...	.	...	...	58·1
30	303·2935	9·0130	0·2052	0·3464	+2·2130	0·0647	33·5
60	234·6171	11·4250	0·3582	0·6244	+4·6080	0·0697	20·5
90	176·8221	13·7840	0·6525	0·0154	+6·9670	0·0736	12·8
120	157·3955	12·8750	0·4375	0·8886	−0·9090	0·0815	12·2

Discussion

Shortly after the commencement of the composting in the buckets the temperature was higher than the surrounding air temperature. The increase of temperature was always higher in the phosphated compost than in unphosphated ones. It was also obs rved that temperature of the set exposed to light was higher than that of the covered set. After 4 to 5 days, signs of decomposition were visible and darkening of the compost had started. Reduction in volume was also observed in all the bucket composts after 45 days.

The sudden rise in temperature indicated that the conditions were favourable for chemical and microbiological decomposition and oxidation. The initial sudden rise in temperature was due to the oxidation of soluble carbohydrates. The continued rise of temperature for a long time indicates that steady oxidation of complex molecules of cellulose and lignin was occurring in the buckets. Waksman and Tenny[11] have reported considerable losses of organic matter in composting. Martin and Wang[12] have observed 80% reduction of organic matter in course of time which shows the rapidity with which it gets oxidized.

Amount of carbon oxidation in the Bucket composts on the addition of different phosphatic fertilizers

Original carbon present 396·46 gms

	Treatments	Days	Carbon oxidised (gms) Light	Dark
1.	KANS (alone)	90	141·53	113·78
2.	KANS + Algerian rock phosphate "A"	90	220·53	162·76
3.	KANS + Algerian rock phosphate "B"	90	206·74	168·10
4.	KANS + Algerian rock phosphate "C"	90	227·57	183·56
5.	KANS + Tata basic slag	90	251·36	211·71
6.	KANS + Kulti basic slag	90	243·03	201·58
7.	KANS + Bihar rock phosphate	90	219·90	162·55
8.	KANS + Trichinopoly rock phosphate	90	224·00	173·25
9.	KANS + superphosphate	90	218·05	175·63
10.	KANS + Belgian basic slag	90	257·50	219·64

It is clear from the above results that carbon was oxidised to a greater extent in the phosphated composts than in the unphosphated ones both in the light and in the dark. During the composting process a progressive increase of nitrogen concentration was observed. The Kans was originally poor in nitrogen content, *i.e.*, 0·6817%. But as the decomposition proceeded, nitrogen concentration increased. This increase in concentration of nitrogen followed the decrease of total organic matter and organic carbon. The increase is due evidently to rapid and continuous losses of organic matter and also partially due to the fixation of atmospheric nitrogen in the composts as is revealed by the total nitrogen values.

Original N Present 6·82 gms.

Treatments		Days	Nitrogen (gms)	
			Light	Dark
1. KANS (alone)		90	11·6410	10·4020
2. KANS + Algerian rock phosphate "A"		90	14·6290	11·8750
3. KANS + ,, ,, ,, "B"		90	15·0270	12·3270
4. KANS + ,, ,, ,, "C"		90	15·5630	12·7520
5. KANS + Tata basic slag		90	16·4730	13·4350
6. KANS + Kulti basic slag		90	16·0580	13·2180
7. KANS + Bihar rock phosphate		90	14·1150	11·5130
8. KANS + Trichinopoly rock phosphate		90	15·2690	12·5640
9. KANS + Superphosphate		90	15·0750	12·3450
0. KANS + Belgian basic slag		90	16·8540	13·7840

From the foregoing results it appears that nitrogen content in the phosphated composts was greater both in light and in the dark than the unphosphated composts. But, an analysis of these composts after 90 days showed some loss of nitrogen. It was also observed that the C/N ratio in the presence of phosphates was lower than in the absence of phosphates.

An increase in nitrogen in the composts by nitrogen fixation from air has been reported by a number of workers. Howard and Wad[13] reported gain in nitrogen from 4·4 to 26·3%. One case in which residues were poor in nitrogen showed the highest nitrogen fixation of 26·3%, but, in most of the experiments of Howard considerable loss of nitrogen took place. Acharya and Co-workers[14] have found that addition of earth to decomposing refuse helps in conservation and fixation of nitrogen.

We have also observed in our experiments that in the presence of finely divided rock phosphate, basic slag and superphosphate, the fixation of atmospheric nitrogen is greater than in the absence of phosphates. There is an appreciable amount of nitrogen fixation in our experiments of composting of KANS when small amounts of phosphatic fertilizers were added.

On the whole it appears that composting of these materials with Belgian basic slag, and Tata basic slag is more profitable from the view point of nitrogen increase.

Under ordinary conditions the proteins present or formed in nitrogen fixation undergo ammonification and nitrification, which are also accelerated by light absorption and increase of temperature and form nitrate as in the following scheme :

$$\text{Proteins} \rightarrow \text{Amino acids} \xrightarrow{+O_2} NH_4 \text{ compounds} \xrightarrow{+O_2} NO_2 \xrightarrow{+O_2} NO_3$$
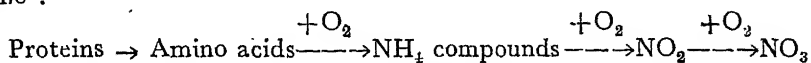
In these series of reactions the unstable substance, ammonium nitrite, is formed and it decomposes according to the following equation.

$$NH_4NO_2 = N_2 + 2H_2O + 718 \text{ K. cals.}$$
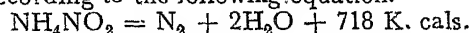
Hence, along with nitrogen fixation and formation of proteins caused by the absorption of energy obtained from the oxidation of energy materials and light absorption in the compost heaps, ammonification and nitrification of the nitrogenous compounds takes place which oppose the increase of amino acids and proteins etc. . . . . in buckets. Thus the amount of proteins remaining in the bucket compost tends to decrease. Consequently, the loss of nitrogen is observed. But, in presence of large amounts of phosphates in the system, stable phospho-proteins are formed by the combination of proteins and phosphates. These compounds seem to resist

ammonification, nitrification and loss of nitrogen as compared to proteins alone. This appears to be an important reason for greater fixation of nitrogen in the phosphated composts.

It has also been observed that there has been greater amount of available phosphate in light than in the dark in all our composting experiments, although, the amount of phosphate added is the same. This is due to the fact that tricalcium phosphate, present in rock phosphate and basic slag, is converted into more soluble forms of phosphate such as dicalcium phosphate and monocalcium phosphate by the action of carbonic acid and other acids produced during the decomposition, ammonification and nitrification of the added organic materials. This is clear from the following equations :

$$(i) \quad Ca_3(PO_4)_2 + CO_2 + H_2O = 2CaHPO_4 \; CaCO_3$$
$$(ii) \quad Ca_3(PO_4)_2 + 2CO_2 + 2H_2O = Ca(H_2PO_4)_2 + 2CaCO_3$$
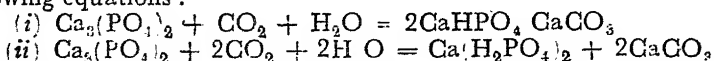
The following observations of Dhar[15] are of great interest in this connection :

"The third dissociation constant of phosphoric acid is smaller than the 1st dissociation constant of carbonic acid and, hence, carbonic acid converts tricalcium phosphate into dicalcium phosphate, which is more soluble than the tricalcium phosphate. Then the availability of phosphates is increased in the systems rich in carbonic acid obtained from the oxidation of organic substances. Similarly, nitrous acid and nitric acid formed in the soil on ammonification and nitrification of proteins make phosphates more readily available. Thus, phosphates are more useful in the presence of organic substances like farm yard manure, straw etc. . . . . undergoing slow oxidation."

In this way more carbonic acid, nitrous and nitric acids become available in the composting of plant materials and convert the tricalcium phosphate and rock phosphate to more soluble form of phosphates such as dicalcium and monocalcium phosphates.

Moreover, we have observed the increased availability of nitrogen in the phosphated and exposed sets than in the unexposed ones, as is evident from the foregoing experimental results.

From the preceding experimental results it is clear that when Kans is composted in conjunction with the phosphates in the presence of light, the nitrogen status of the composts is improved and thus can be utilized profitably in improving the land fertility permanently.

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Effect of different organic materials and phosphate on the yield of Paddy Grain and Paddy Straw, Wheat Grain and Wheat Straw in field trials

By

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The present paper deals with the results obtained by ploughing in different organic materials like wheat straw, Kans (Saccharum spontaneum) and sunhemp (Crotalaria juncia) alone and in conjunction with Tata basic slag (Thomas) on the yield of paddy grown in July 1961 on the same land, without further treatment, wheat was grown in October, 1961.

Methods and Materials

The field trials were conducted at Anapur (Allahabad) in a farmer's field which is uniform. The experience of the resident farmers was utilized in the selection of the site. Soil samples were taken out from the different layers and from different spots upto the depth of 6″ in order to determine the uniformity of the soil of the field. The soil of the field was of the alluvial type in which the crops were continuously grown for a number of years.

The design adopted was randomised block layout, giving six replications to each treatment. The area of each plot was 726 sq. ft., which is just equivalent to 1/60th of an acre. The following organic materials were used as manure :

(1) Wheat straw, (2) Kans (Saccharum spontaneum), (3) sunhemp (Crotalaria juncia). The source of phosphate was Tata Basic slag.

The treatments were as follows :

(*i*) Soil alone (control).

(*ii*) Soil + Wheat straw

(*iii*) Soil + Wheat straw + Phosphate

(*iv*) Soil + Kans

(*v*) Soil + Kans + Phosphate

(*vi*) Soil + Sunhemp

(*vii*) Soil + Sunhemp + Phosphate

Design of the experiment

(*a*) Randomised block layout

Number of treatments	7
Number of replications	6
Number of plots	42

(*b*) *Area of the Plot* 1/60th of an acre (33 ft. 22 ft.)

(c) *Rate of the addition of the amendments per acre* :

      Organic materials   10 tons

      Phosphate as Tata basic slag   50 lbs

(d) *Place*—Anapur (Allahabad District).

(e) *Period of decomposition of the amendments in the pl ts* :

      From 20th April to 2nd July, 1961.

(f) *No. of ploughing during the decompositiou* – 6

      Soil samples were taken before transplanting paddy on 1st July, 1961.

      Soil samples were taken after the harvesting of the crop on 4th October, 1961.

      Date of transplanting paddy   3rd July, 1961.

      Date of harvesting paddy   4th October, 1961.

After harvesting paddy, wheat was sown in the same field to determine the residual effect of the above organic materials and phosphates on the yield of wheat grain and straw.

Canal water was used for irrigation of the paddy and wheat crops.

TABLE 1

Chemical composition of energy materials (oven dried)

	Kans %	Wheat straw %	Sunhcmp %	Soil %
Loss on ignition	91·51	91·08	89·84	3·86
Ash	8·48	8·84	10·16	96. 16
HCl insoluble	4·68	5·38	5·88	82·30
Sesquioxide	0·8740	1·43	0·7246	11·18
Fe_2O_3	0·3253	0·6015	0·2946	4·13
CaO	0·7726	0·7439	1·20	0·9871
P_2O_5	0·5283	0·5432	0·8277	0·0787
K_2O	0·8975	0·5793	0·7462	0·9782
MgO	0·6827	0·1510	0·4362	0·3583
Available P_2O_5 (1% citric acid solution)	–	–	–	0·0104
Total carbon	39·64	36·70	22·65	0·5475
Total nitrogen	0·6817	0·6015	0·8625	0·0558
$NH_3 - N$	–	–	–	0·0048
$NO_3 - N$	–	–	–	0·0063
C/N ratio	58·1	61·0	26·2	10·8

Tata Basic slag contains 7·5% P_2O_5.

TABLE 2

Composition of soil before paddy transplantation

Constitutionals	Soil alone (control)	Soil + wheat straw 10 tons/acre	Soil+wheat straw 10 tons/acre + P_2O_5 as T.B.S. (50 lbs/acre)	Soil + Kans 10 tons/acre	Soil + Kans 10 tons/acre + P_2O_5 as T.B.S.(50 lbs/acre)	Soil + sun-hemp 10 tons/acre	Soil+sun-hemp 10 tons/acre+ P_2O_5 as T.B.S. (50 lbs/acre)
Sesquioxide %	11·18	11·21	11·42	11·19	11·35	11·18	11·26
Ironoxide %	4·13	4·15	4·26	4·14	4·21	4·13	4·19
Total CaO %	0·9872	1·1231	1·4263	1·0985	1·3545	1·0621	1·2626
Total P_2O_5 %	0·0782	0·0823	0·2534	0·0809	0·2262	0·0799	0·2048
Av. P_2O_5 (1% citric acid solution)	0·0159	0·0213	0·0625	0·0196	0·0526	0·0185	0·0575
Total K_2O	0·9785	1·0152	1·1274	1·0095	1·0973	1·0036	1·0672
Total MgO	0·5592	0·5826	0·6265	0·5626	0·6083	0·5672	0·5727
Total Carbon %	0·5466	0·8243	0·6476	0·8077	0·6621	0·6821	0·5853
Total Nitrogen %	0·0554	0·0942	0·1272	0·0834	0·1154	0·0862	0·1046
NH_3—N %	0·0046	0·0135	0·0157	0·0126	0·0148	0·0122	0·0136
NO_3—N %	0·0064	0·0154	0·0265	0·0148	0·0225	0·0135	0·0196
C/N ratio	10·8	8·7	5·0	9·1	5·7	7·9	5·6

TABLE 3

Chemical composition of soil after harvesting of paddy crop

Constitutionals	Soil alone (control)	Soil + wheat straw 10 tons/acre	Soil+wheat straw 10 tons/acre + P_2O_5 as T.B.S. (50 lbs/acre)	Soil + Kans 10 tons/acre	Soil + Kans 10 tons/acre + P_2O_5 as T.B.S.(50 lbs/acre)	Soil + sun-hemp 10 tons/acre	Soil+sun-hemp 10 tons/acre+ P_2O_5 as T.B.S. (50 lbs/acre)
Sesquioxide	11·15	11·18	11·30	11·17	11·20	11·16	11·18
Ironoxide %	3·66	3·96	4·05	3·88	3·99	3·72	3·87
Total CaO %	0·9882	1·0045	0·2652	0·9959	1·1246	0·9866	1·1065
Total P_2O_5 %	0·0762	0·0784	0·2267	0·0796	0·2076	0·0786	0·1885
Av. P_2O_5 (1% citric acid solution) %	0·0142	0·0246	0·0675	0·0214	0·0566	0·0208	0·0539
Total K_2O %	0·9552	0·9862	1·0087	0·9825	1·0076	0·9845	1·0065
Total MgO %	0·5463	0·5615	0·5847	0·5602	0·5672	0·5596	0·5648
Total carbon %	0·5436	0·6842	0·5865	0·6687	0·6056	0·6078	0·5606
Total nitrogen %	0·0543	0·0836	0·1027	0·0805	0·0943	0·0783	0·0874
NH_3—N	0·0042	0·0146	0·0164	0·0138	0·0156	0·0132	0·0144
NO_3—N	0·0058	0·0167	0·0272	0·0158	0·0233	0·0146	0·0206
C/N ratio	10·0	8·1	5·7	8·3	6·8	8·1	6·4

TABLE 4
Yield paddy grains in Kgs.

Treatments	Blocks 1	2	3	4	5	6	Total
Soil alone (control)	11·50	12·25	10·75	11·00	13·00	10·25	68·75
Soil+wheat straw 10 tons/acre	18·00	17·25	19·50	16·50	18·50	18·25	108·00
Soil + wheat straw 10 tons/ acre + P_2O_5 as T.B.S. (50 lbs/ acre)	23·25	22·75	23·50	24·50	21·50	23·50	139·00
Soil + Kans 10 tons/acre	16·75	15·50	16·25	17·75	15·00	16·00	97·25
Soil + Kans 10 tons/acre + P_2O_5 as T.B.S. (50 lbs/acre)	21·75	21·25	22·25	22·75	20·50	21·25	129·75
Soil + sunhemp 10 tons/acre	15·50	14·75	16·75	15·25	15·75	16·00	94·00
Soil + sunhemp 10 tons/acre + P_2O_5 as T.B.S. (50 lbs/acre)	18·75	19·25	17·50	18·50	19·50	18·50	112·00
Total	125·50	123·00	126·50	126·25	123·75	123·75	784·75

TABLE 5
Analysis of variance for the yield of paddy grains

Sources of variation	D.F.	S.S.	M.S.	F. Calculated	F. from table 1%	5%	Level of significance
Total	41	567·3111	13·8368	—	—	—	Yield is highly
Blocks	5	1·5611	0·3122	0·05	3·70	2·53	Significant
Treatments	6	382·4465	63·7410	10·4	3·47	2·42	
Error	30	183·3035	6·1101	—	—	—	

TABLE 6
Yield of Paddy straw in Kgs

Treatments	Blocks 1	2	3	4	5	6	Total
Soil alone (control)	30	29	28	25	29	27	168
Soil + wheat straw (10 tons/acre)	52	48	50	47	53	51	301
Soil + wheat straw (10 tons/acre) + P_2O_5 as T. B. S. (50 lbs/acre)	65	62	67	63	68	64	389
Soil + Kans (10 tons/acre)	45	47	48	46	44	45	275
Soil + Kans (10 tons/acre) + P_2O_5 as T. B. S. (50 lbs/acre)	60	63	59	64	62	60	368
Soil + sunhemp (10 tons/acre)	42	43	39	40	44	42	250
Soil + sunhemp (10 tons/acre) + P_2O_5 as T. B. S. (50 lbs/acre)	54	53	55	56	52	51	321
Total	348	345	346	341	352	340	2072

TABLE 7

Analysis of variance for the yield of Paddy straw

Sources of variation	D. F.	S. S.	M. S.	F. Calculated	F. from table 1%	F. from table 5%	Level of significance
Total	41	5705·0	139·1	—	—	—	Yield is
Block	5	14·2	2·84	0·22	3·70	2·53	highly
Treatments	6	5304·0	884·0	69·0	3·47	2·42	significant
Error	30	30	386·8	12·8	—	—	

TABLE 8

Yield of wheat grains in Kgs

Treatments	1	2	3	4	5	6	Total
Soil alone (control)	8·25	10·50	9·25	8·0	10·50	10·0	56·50
Soil + wheat straw (10 tons/acre)	13·25	13·25	63·50	13·0	14·20	14·50	82·00
Soil + wheat straw 10 tons/acre + P_2O_5 as T. B. S. (50 lbs/acre)	19·25	18·50	20·00	17·50	19·00	17·25	111·50
Soil + Kans 10 tons/acre	12·50	13·00	11·50	14·00	12·25	13·25	76·50
Soil + Kans 10 tons/acre + P_2O_5 as T. B. S. (50 lbs/acre)	16·25	17·50	15·50	17·25	18·00	16·00	100·50
Soil + sunhemp 10 tons/acre	11·50	11·50	12·75	11·50	10·25	11·50	69·00
Soil + sunhemp 10 tons/acre + P_2O_5 as T. B. S. (50 lbs/acre)	15·75	14·25	15·75	16·00	15·25	15·50	92·50
Total	96·75	98·50	38 25	97·25	99·75	98·00	588·50

TABLE 9

Analysis of variance for the yield of wheat grains

Sources of variation	D. F.	S. S.	M. S.	F. Calculated	F. from table 1%	F. from table 5%	Level of significance
Total	41	382·5	9·3	—	—	—	Yield is
Block	5	0·8	0·16	0·17	3·70	2·53	highly
Treatment	6	353·7	59·9	66·5	3·47	2·42	significant
Error	30	28·5	0·9	—	—	—	

| Treatments | Blocks | | | | | | Total |
	1	2	3	4	5	6	
Soil alone (control)	20	18	17	21	19	20	115
Soil + wheat straw 10 tons/acre	31	32	30	33	32	33	191
Soil + wheat straw 10 tons/acre + P$_2$O$_5$ as T. B. S. (50 lbs/acre)	40	42	43	40	42	43	250
Soil + Kans 10 tons/acre	28	29	30	32	30	31	180
Soil + Kans 10 tons/acre + P$_2$O$_5$ as T. B. S. (50 lbs/acre)	37	40	39	38	39	38	231
Soil + sunhemp 10 tons/acre	27	26	28	29	25	25	160
Soil + sunhemp 10 tons/acre + P$_2$O$_5$ as T. B. S. (50 lbs/acre)	32	34	33	31	32	32	194
Total	215	221	220	224	219	222	1321

TABLE 11
Analysis of variance for the yield of wheat straw

Sources of variation	D. F.	S. S.	M. S.	F calculated	F from table 1%	F from table 5%	Level of significance
Total	41	2030·4	49·7	–	–	–	
Block	5	11·4	2·28	2·0	3·70	2·53	Yield is
Treatment	6	1985·2	300·7	3·47	2·42	–	highly signi-
Error	30	33·8	1·1	–	–	–	ficant.

Discussion

From the preceding results it is evident that by the addition of different organic materials like wheat straw, Kans and sunhemp (as green manure) at the rate of 10 tons per acre to the field, much better results were obtained than in the 'control' in which no organic matter was added. A good amount of increase in the yield of paddy grain and straw was obtained in the 1st year of application and also a good yield of wheat grain and straw was obtained in the succeeding season of crop. Moreover, when phosphate was incorporated with these organic materials at the rate of 50 lbs per acre of P$_2$O$_5$ as Tata basic slag, still better results were obtained than the treatment in which phosphate was not added. The effect of different phosphated organic materials on the yield of paddy grain, paddy straw, wheat grain and wheat straw was in the following decreasing order :

Phosphated wheat straw > Phosphated Kans > Phosphated sunhemp.

The same order in the yield of grain and straw was also observed when only organic materials were added at the rate of 10 tons per acre to the field.

It has been noticed in these field trials that there is greater increase in the yield of paddy grain, wheat grain, paddy straw and wheat straw when organic materials are incorporated with phosphate than without phosphate. These marked difference in the yield of grain and straw may be due to the presence of higher amounts of total nitrogen and available nitrogen. It has been obtained

from the analysis of the soil after the decomposition and before the transplantation of paddy that the plots which were treated with organic material and phosphate contained greater amount of total and available nitrogen and available phosphate than the plots which were treated with organic materials only.

It has been found in several experimental results of Dhar and co-workers[1] that a mixture of organic substances like farm yard manure, straw, plant residues etc. and calcium phosphate, when incorporated in the soil, can build up soil fertility permanently by fixing atmospheric nitrogen and supply available nitrogen, phosphate, potash, trace-elements and humus and thus maintain soil fertility.

Moreover, many workers have reported a marked beneficial effect of a mixture of plant residues and rock phosphate in crop production. Our results also prove the same because higher yields of grain and straw of both paddy and wheat were obtained in the case of plots which were treated with phosphate and organic matter.

In our field trials, the plots, which have been treated with wheat straw alone, as well as with a mixture of wheat straw and phosphate gave out the highest yields of grain and straw in both the cases i.e., of Paddy and wheat. It seems, therefore, that the addition of wheat straw alone. as well as wheat straw and phosphate is better than the other treatments. The reason may be due to the higher content of lignin in wheat straw than in Kans and sunhemp, because, lignin forms stable ligno-proteins and thus the loss of nitrogen is decreased during composting. Peevy and Norman[2] have observed that the soil receiving more resistant materials like lignin had a higher content of nitrogen. We have also found in our trials that higher amount of nitrogen was fixed in the following order :

Phosphated wheat straw > Phosphated Kans > Phosphated sunhemp

The lowest yield next to 'control' was obtained in the sunhemp treated plots; sunhemp in green stage contains less carbonaceous materials. It appears, therefore, that a certain amount of lignin is helpful in maintaining and improving the nitrogen status of the soil. Gaur[3] has found that by the composting of lignin-rich materials like saw dust, and wheat straw, greater conservation of nitrogen was observed.

Similarly in Europe, the value of organic matter in soil fertility has been emphasised by Demolon and Burgevin working in France for a number of years and beneficial results were obtained by ploughing in straw. Cooper[4] found that uncomposted materials could be applied to land with beneficial results. Eden[5] as well has carried out some experiments successfully with uncomposted refuse.

Dhar[6] has concluded that organic compounds not only fix atmospheric nitrogen, but they contain and add colloidal substances to the soil, improve the tilth, crumb formation, and water retention capacity of the soil.

From the foregoing, field trials we come to the conclusion that direct application of the organic materials along with phosphate ploughed in the soil, certainly increases the land fertility considerably and increased yields are thereby obtained.

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Influence of Basic slag, Organic Materials and Algae on Soil Fertility

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Abstract

Tata basic slag (powdered) at the rate of 50 lbs of P_2O_5 per acre was applied along with Kans (Saccharum spontaneum) at the rate of 10 tons per acre in the soil in field trial conducted at Varanasi. Three algae *viz.*, Anabaena naviculoides, Tolypothrix tenuis and Chlorella vulgaris were also inoculated in the soil treatments.

Application of the Tata basic slag increased the rate of oxidation of organic materials and thus helped in the availability of soil nutrients. Paddy crop was transplanted after two months application of organic materials and the yield of the harvest was also recorded. The recovery and residual nutrient status of the soil treatments were tabulated and it has been observed that the residual nutrient status of soil increased.

All kinds of organic matter irrespective of whether applied as farm manure, compost, peat, straw, sawdust, dung, leaves or molasses undergo slow oxidation in soil aided by light absorption and oxygen of air, forming humus. Humus has an intimate relation with fertilizing properties of the soil. Dhar and coworkers[1] have been able to prove that organic matter incorporated to the soil undergoes slow oxidation in presence of air, liberating energy. This energy is utilised in fixing atmospheric nitrogen more in presence of light than in dark.

Numerous investigators, Lipman and Blair[2] have proved that organic matter and nitrogen supply of the soil can be maintained only by the use of stable manures or green manures. Dhar[3] in his presidential address to the National Academy of Sciences, India, has emphasized that the direct application of plant materials to the fields before composting is more beneficial to the crops, because the energy materials like carbohydrates, lignins, fats, etc., when added to the soil, are partially oxidised and in this process nitrogen of the air is fixed. The method of direct application of plant materials to soil without composting has been adopted in farms of Sweden, England and in Pennsylvania and California, U. S. A.

Phosphate fertilizers improve the fertility of the soil is an universally acclaimed fact. A very extensive research work is being carried on the use of phosphates especially basic slags, in land fertility improvement all over the world particularly in Europe [4,5,6,7]. it is postulated [8,9,10,11,12,13] that blue green algae of the family Nostocacae including members of genera Nostoc, Anabaena, Aulosira and Cylindrospermum, can fix the nitrogen of the air.

In order to throw further light on above facts a field trial was conducted by using Kans (Saccharum spontaneum) along with Tata basic slag and bule green algae were also inoculated.

Methods and Materials

The field trials were carried out at Hathiar (Varanasi) U. P. The land selected for these experiments was as uniform as possible and this minimised the effect of soil fertility differences between he plots. Soil samples were collected and analysed from different spots upto the depth of 0–9 inches in order to determine the uniformity of the soil. The soil was sandy loam (alluvial type). The field was ploughed, chapped Kans (Saccharum spontaneum) and Tata basic slag (powdered) were mixed in some plots in the month of June. The field was k pt moistened with irrigation water till rains started and four ploughings were given before transplanting paddy in order to facilitate the oxidation and decomposition of the straw.

The inoculation of rice field water by algae was performed during the period from June to August. Before transplanting paddy seedlings (Variety N 22), soil samples were taken out for each plot for analysis. No other fertilizer was added during the growing season.

Kans was applied at the rate of 10 tons per acre. Tata basic slag was applied at the rate of 50 lbs. of P_2O_5 per acre.

Total No. of plots $= 16 \times 3 = 48$
(treatments $= 16$ and replications 3)

Size of the plots $= 1/60$th acre i.e. ($33' \times 22'$)

Paddy Variety grown $= N\ 22$

Randomized block design was followed.

TABLE 1

Chemical composition of soil, Kans and Tata basic slag (TBS) in percentage on oven dried basis

	Soil	Kans	T. B. S.
Loss on ignition	4.9540	86.521	—
HCl (insoluble)	78.140	5.380	16.00
Sesquioxides	7.820	0.833	—
Fe_2O_3	3.856	0.331	15.286
Total P_2O_5	0.1380	0.408	7.16
Total CaO	0.8947	0.732	38.79
Total K_2O	0.9446	0.901	0.65
Total MgO	0.4372	0.632	4.79
Total carbon	0.6013	39.165	—
Total Nitrogen	0.0578	0.6913	—
C/N ratio	10.4	57.3	—
Avail, P_2O_5	0.0186	—	4.05
Avail. N	0.0058	—	—
pH	7.5	—	—

[481]

Results and Discussion

TABLE 2

Composition of soil (percent) before transplanting paddy seedlings (Average of 3 plots)

Treatments	Total C	Total N	Total P_2O_5	K_2O	MgO	CaO	Avail. N	Avail. P_2O_5
Control	0·5780	0·0562	0·1325	0·6283	0·4350	0·8766	0·0048	0·0169
Kans	0·6512	0·0745	0·1405	0·6710	0·4606	0·9028	0·0075	0·0229
T.B.S.	0·5428	0·0586	0·1527	0·6299	0·4365	0·8790	0·0058	0·0370
Kans + T.B.S.	0·6070	0·0817	0·1640	0·6384	0·4823	1·0263	0·0128	0·0528

Average yields of paddy grain and straw obtained from different treatments are recorded below.

TABLE 3

Treatments	Average yield of paddy in Kgs.	
	Grain yield/ plot	Straw yield/ plot
Control	10·7	18·5
Chlorella	10·9	19·0
Anabaena	11·4	19·7
Tolypothrix	11·9	20·5
Kans	15·7	23·0
Kans + Chlorella	16·0	28·7
Kans + Anabaena	16·6	30·6
Kans + Tolypothrix	17·1	31·3
T.B.S.	12·8	22·2
T.B.S. + Chlorella	13·1	24·1
T.B.S. + Anabaena	13·9	25·7
T.B.S. + Tolypothrix	14·2	26·4
Kans + T.B.S.	20·0	37·5
Kans + T.B.S. + Chlorella	20·3	38·2
Kans + T.B.S. + Anabaena	21·5	39·0
Kans + T.B.S. + Tolypothrix	22·7	39·3

(Plot size = 1/60th acre)

TABLE 4

Composition of soil (percent) after harvest of paddy crop (Average of 3 plots)

Treatments	Total carbon	Total nitrogen	Total P₂O₅	K₂O	MgO	CaO	Avail. N	Avail P₂O₅.
Control	0·5665	0·0534	0·1297	0·6206	0·4307	0·8656	0·0046	0·0143
Chlorella	0·5668	0·0534	0·1295	0·6204	0·4305	0·8653	0·0037	0 0141
Anabaena	0·5666	0·0535	0·1295	0·6205	0·4305	0·8655	0·0038	0·0142
Tolypothrix	0·5667	0·0535	0·1296	0·6204	0·4306	0 8654	0·0038	0·0141
Kans	0·5463	0·0647	0·1355	0·6467	0·4444	0·8692	0·0049	0·0240
Kans + Chlorella	0 5466	0·0647	0·1352	0·6465	0·4442	0·8690	0·0051	0·0237
Kans + Anabaena	0·5464	0·0649	0·1353	0·6464	0·4443	0·8689	0·0052	0·0238
Kans + Tolypothrix	0·5465	0·0650	0·1354	0·6465	0·4442	0·8690	0·0052	0·0239
T.B.S.	0·5180	0·0554	0·1368	0·6303	0·4324	0·8692	0·0047	0·0529
T.B.S. + Chlorella	0·5183	0·0555	0·1366	0·6201	0·4322	0·8690	0·0049	0·0526
T.B.S. + Anabaena	0·5182	0·0556	0·1366	0·6302	0·4323	0·8690	0·0051	0·0227
T.B.S. + Tolypothrix	0·5181	0·0556	0·1365	0·6302	0·4322	0·8689	0·0050	0·0527
Kans + T.B.S.	0·4800	0·0704	0·1532	0·6760	0·5182	0·9418	0·0096	0·0557
Kans + T.B.S + Cholrella	0·4804	0·0704	0·1530	0·6757	0·5179	0·9415	0·0098	0 0554
Kans + T.B.S. + Anabaena	0·4802	0·0705	0·1531	0·6758	0·5180	0·9416	0·0100	0·0555
Kans + T.B.S. + Tolypothrix	0·4801	0·0706	0·1530	0·6759	0·5181	0·9415	0·0101	0·0556

From the foregoing results it is clear that the organic materials when added directly produces better yield when incorporated with Tata basic slag. From the Table No. 3 the yield of paddy grain (Variety N 22) and straw due to inoculation of algae are summarized below :

Due to	Increase of paddy grain and straw in kgs pre acre over control	
	Paddy grain (kgs)	Paddy straw (kgs)
1. Chlorella	12·0	30·0
2. Anabaena	42·0	72·0
3. Tolypothrix	72·0	120.0
4. Kans	300·0	270·0
5. T.B.S.	126·0	222·0
6. Kans + T.B.S.	558·0	1140·0
7. Kans+T.B.S. + Chlorella	576·0	1182·0
8. Kans+T.B.S + Anabaena	648·0	1250·0
9. Kans+T.B.S. + Tolypothrix	720·0	1248·0

Dhar and his associates[14] after carrying out a large number of pot and field experiments have concluded from their observations that a greater yield of paddy and other crops is influenced by applying organic materials and phosphates. Watanabe[15] of Japan also obtained in the first year about 5% increase with inoculation of Tolypothrix tenuis. An examination of data on the soil analysis recorded in Table No. 2 and 4 indicate that in all cases there was a decrease of carbon and nitrogen of the soils after the harvest of the paddy crops. However there is slightly more carbon and nitrogen in the inoculated plots than in the non-inoculated ones. This is due to fixation of atmospheric nitrogen by algae organic matter which adds carbonaceous compounds to the soil.

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Fixation of Nitrogen in presence of Pure Oxide Surfaces by the slow oxidation of energy materials

By

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Large quantities of nitrogen as nitrogenous compounds are removed every year from soil by growing crops and by the action of several groups of soil micro-organisms. The quantities of manure returned to the soil are far from adequate to replace this loss and the attempt to replace this loss by artificial fertilisers may be adequate to supply the need of the growing plant but not to replenish the losses from the soil ; so there must be some mechanism of nitrogen fixation in soil that counter balances the above nitrogen depletion.

The reactions causing nitrogen fixation in soil have been attributed to :

(1) Certain microorganisms, some of which function non symbiotically while others function in symbiosis with plants and

(2) Certain blue green algae of the family Nostococaceae.

Though it has been advocated by a large number of workers that the phenomenon of nitrogen fixation in soil is essentially a microbiological process[1] but still the amount of nitrogen fixed under non symbiotic condition is considered to be negligible by workers like Russell[2], Waksman[3] and Miller[4].

Dhar and Coworkers[5] have however shown in a number of publications that when different energy producing materials like sugars, glycerol, starch, cowdung, peat etc. undergo slow oxidation in air in presence of soil or sand both under sterile and unste.ile conditions, along with carbon oxidation there is appreciable fixation of atmospheric nitrogen which is always greater in light than in dark.

For better study and understanding experiments were carried out using chemically pure oxide surfaces like Titania, Zinc oxide and ferric oxide instead of soil or sand mixed with energy materials like glucose and sta ch. In this case the systems were simple as they were devoid of the complexities of soil and were also initially free of nitrogen. The influence of phosphates on the above system were also studied by using dicalcium phosphate.

Experimental Procedures

Oven dried and sieved titania was weighed into a number of conical flasks (5 gms of titania in each flask). Into each of these flasks 200 c. c. of glucose solution containing one per cent carbon as glucose were added. Then weighed amount of dicalcium phosphate (corresponding to 0.5% P_2O_5) was added to half the flasks. All these flasks were plugged with cotton wool and exposed to light from a 100 watt electric blub for 6–8 hours daily. An identical set of flasks was next prepared, covered with a thick black cloth to cut off all light and placed alongside the exposed flasks.

The above method was then repeated using titaina as surface and solutions containing 2% carbon as glucose, 1% carbon as starch and 2% carbon as starch respectively. In every case 5 gms of titania were used as surface and 200 c.c. of glucose solution or starch suspension was introduced into each flask.

For the sterile sets the entire above process was repeated then all the flasks sterilised for 20–30 minutes at 15 lbs pressure and 110°C before exposing to light.

The process was next repeated using 5 gms of oven dried and sieved zinc oxide and ferric oxide as surface respectively. In every case sterile and unsterile sets were prepared and half the exposed and half the covered sets had 0·5% as P_2O_5 as dicalcium phosphate.

The flasks were shaken daily for a few minutes.

After definite intervals of time the contents of one flask from each set (sterile, unsterile, exposed and covered) was transferred to a pestle, well ground and transferred into a 250 c. c. volumetric flask and the volume made up. An aliquot portion was then taken, evaporated on the water bath with a drop of concentrated sulphuric acid to prevent the escape of any ammonia and analysed for total carbon by the method of Robinson Mclean and Williams and for total nitrogen by the Kjeldahl method as modified by Treadwell and Hall.

At the time of each analysis the contents of a sterile flask from each sterile set was tested for complete sterility by the following method : the sterile flask was opened, samples of the contents were inoculated into a series of sterile microbial growth media and after slopes. These were then sealed and incubated for two weeks at 37°C. If no growth was detected in any medium or any slope it was taken as an indication of complete absence of microbial contamination of the flasks.

Experimental Results

TABLE 1
5 gms Titania + 1% carbon as glucose   *Unsterile*

Period of exposure in days	Total carbon unoxidised gm	Total Nitrogen mgm	Efficiency	Percentage carbon oxidation	C/N Ratio
			Light		
0	2·0000	—	—	—	—
30	1·7438	14·50	56·6	12·61	120·2
60	1·5820	23·18	55·5	20·90	68·2
90	1·4854	27·80	54·2	25·73	53·4
120	1·4300	30·02	52·7	28·50	44·3
			Dark		
0	2·0000	—	—	—	—
30	1·8104	6·92	40·8	8·48	264·5
60	1·7196	11·22	40·0	14·02	153·4
90	1·6578	13·34	39·0	17·11	124·3
120	1·5868	14·81	37·9	20·66	107·2

TABLE 2

5 gms Titania + 1% carbon as glucose + 5% P_2O_5 as $CaHPO_4$ $2H_2O$ Sterile

Period of exposure in days	Total carbon unoxidised gm	Total Nitrogen mgm	Efficiency	Percentage carbon oxidation	C/N Ratio
Light					
0	2·0000	—	—	—	—
30	1·6792	22·12	69·0	16·07	75·9
60	1·4958	34·32	68·1	25·21	43·5
90	1·3840	41·26	67·0	30·80	33·5
120	1·3090	45·46	65·8	39·55	28·7
Dark					
0	2·0000	—	—	—	—
30	1·7842	10·10	46·3	10·79	176·6
60	1·6608	13·46	45·6	16·96	123·3
90	1·5960	18·04	44·7	20·20	88·4
120	1·5384	20·17	43·7	23·08	76·3

TABLE 3

5 gms Titania + 1% carbon as glucose

Light					
0	2·0000	—	—	—	—
30	1·8720	5·38	45·5	6·40	347·9
60	1·7958	9·14	44·7	10·21	196·4
90	1·7475	11·06	43·2	12·63	157·9
120	1·7219	11·96	43·0	13·91	143·9
Dark					
0	2·0000	—	—	—	—
30	1·9432	1·63	28·7	2·84	1192·1
60	1·9013	2·80	28·5	4·93	679·0
90	1·8799	3·36	28·0	6·01	559·4
120	1·8664	3·68	27·5	6·68	507·1

TABLE 4

5 gms Titania + 1% carbon as glucose + 0·5% P_2O_5 as $CaHPO_4$ $2H_2O$

Light					
0	2·0000	—	—	—	—
30	1·8476	8·26	54·1	7·62	223·6
60	1·7539	13·18	53·5	12·31	123·0
90	1·7001	15·76	52·7	15·00	107·8
120	1·6658	17·32	51·8	16·71	96·1
Dark					
0	2·0000	—	—	—	—
30	1·9292	2·42	34·5	3·04	797·1
60	1·8623	4·02	34·0	5·89	468·2
90	1·8523	4·90	33·3	7·36	378·1
120	1·8397	5·24	32·6	8·01	351·1

TABLE 5

Percentage of carbon oxidised after 120 *days*

	Unsterile		Sterile	
	Exposed	Covered	Exposed	Covered
Titania + 1% carbon as glucose	28·50	20·66	13·91	6 68
Titania + 2% carbon as glucose	26·22	17·31	12·81	6·05
Zinc Oxide + 1% carbon as glucose	23·06	15·99	10·61	4·80
Zinc Oxide + 2% carbon as glucose	21·30	14·23	9·50	4·64
Ferric Oxide + 1% carbon as glucose	20·73	13·93	9·86	4·64
Ferric Oxide + 2% carbon as glucose	19·44	12·99	9·00	4·42
Titania + 1% carbon as starch	23·23	15·81	11·41	5·08
Titania + 2% carbon as starch	21·40	13·92	10·61	5·02
Zinc Oxide + 1% carbon as starch	18·36	11·98	8·31	3·80
Zinc Oxide + 2% carbon as starch	16·41	11·00	7·07	3·23
Ferric Oxide + 1% carbon as starch	15·50	11·20	6·91	3 20
Ferric Oxide + 2% carbon as starch	14·31	9·25	5·60	2·61

Discussion

It was observed that when energy materials like glucose and starch were mixed with metallic oxides and exposed to air there was a decrease in the carbon content of the system with concomitant fixation of nitrogen both under sterile and unsterile conditions. The percentage of oxidation of carbon under sterile conditions both in case of glucose and starch in the exposed sets was found to be a little less than half that in the corresponding exposed sets under unsterile conditions and the percentage of oxidation of carbon in the covered sets under sterile conditions was found to be approximately one third of the carbon oxidation in the covered sets under unsterile conditions as is clear from table 5. These results bring out the marked significance of surface and light in oxidation reactions as the oxidation of carbon in the sets exposed to light under unsterile conditions is a combination of microbial, photochemical, surface and catalytic reactions, while that in the corresponding sets under sterile conditions is a total of photochemical, surface and catalytic reactions. Similarly the oxidation of carbon in the covered sets under unsterile conditions is a combination of microbial surface and catalytic reactions while that in the corresponding sterile sets is purely a surface and catalytic reaction.

As far as the surfaces were concerned regarding the rate of oxidation of carbon, fixation of atmospheric nitrogen and efficiency *i.e.* the amount of nitrogen fixed in mgms. per gm. of carbon oxidised, the activity was found to be of the following order.

Titania > Zinc Oxide > Ferric oxide.

both under sterile and unsterile conditions and this difference with the three surfaces seems to be due to their power in photosensitization.

The efficiency of nitrogen fixation was seen to fall off with the lapse of time. This gradual decrease in the efficiency may be explained by the fact that even in soil the process of nitrogen fixation is always opposed by that of ammonification and nitrification by which the proteins and amino acids formed are oxidised in the following manner.

$$\text{Proteins} \longrightarrow \text{amino acids} \xrightarrow{+O_2} \text{ammonium compourds} \xrightarrow{+O_2} NO_2 \xrightarrow{+O_2} NO_3$$
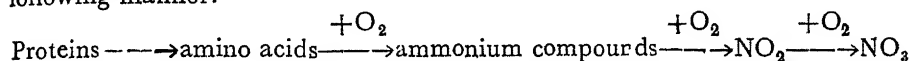
In this series of reactions the unstable and explosive substance ammonium nitrite is formed which readily undergoes decomposition as follows :

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O + 718 \text{ K. cals.}$$
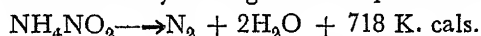
liberating energy, nitrogen and water. Consequently the efficiency of nitrogen fixation falls off.

The addition of dicalcium phosphate was observed to increase the efficiency of nitrogen fixation and also check the rate of fall in the efficiency of nitrogen fixation. This is presumably due to the fact that in presence of dicalcium phosphate containing Ca^{++} ions the more stable compound calcium nitrite is formed instead of ammonium nitrite. Dhar and Ghosh[6] from a study of the physical properties like the depression in freezing point, elevation in boiling point and electrical conductivity measurements, have established the possibility of the formation of phosphorylated compounds in vitro when phosphoric acid is mixed with amino acids, adenine etc. These compounds seem to resist ammonification, nitrification and the loss of nitrogen better than proteins and amino acids. Thus, coupled with the observation that dicalcium phosphate enhances the oxidation of carbon and a part of the nitrogen may be fixed due to the release of the extra energy appears to be a plausible reason why the efficiency of nitrogen fixation appears higher in the phosphated sets.

The C/N ratio was observed to gradually decrease with the lapse of time and this decrease was always greater in light than in dark under both sterile and unsterile conditions. Also the C/N ratio was always found to be smaller in the sets containing dicalcium phosphate as compared to the corresponding sets without it. This again shows that phosphates not only increase the efficiency of nitrogen fixation but also stabilise the nitrogen fixed.

In explaining photosynthesis in plants, Dhar[7] postulated in 1933 that the important photochemical reaction is the decomposition of water by the absorption of light according to the following equation :

$$H_2O + 112 \text{ K. cal} = H + OH$$
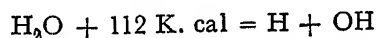
The hydrogen atom thus formed reduces the carbonic acid absorbed on the leaves forming formeldehyde. In recent years this view of the mechanism of photosynthesis has been supported by the use of carbonic acid containing isotopic carbon.

[489]

We have to assume that in nitrogen fixation in soils and on pure oxide surfaces, a breaking up of water molecules into atomic hydrogen is the fundamental process.

Thus in explaining nitrogen fixation the best mechanism seems to be the photolysis of water into H and OH by the absorption of energy obtained by the oxidation of carbohydrates etc. followed by the chemical combination of this atomic hydrogen with atmospheric nitrogen leading to the formation of ammonia :

$$N_2 + 6H = 2NH_3$$
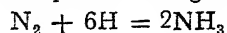
It seems that the fixed nitrogen in the form of ammonia, or which might later change to nitrite and nitrate in presence of light and air, interacts with the unoxidised energy materials as well as the intermediate products obtained producing amino acids. Moreover in presence of light, the light energy, solar or artificial is absorbed by the system and utilised in increasing the fixation of nitrogen.

Thus the results of the experiments carried out show that nitrogen fixation is possible with chemically pure metallic oxides as surfaces both under sterile and unsterile conditions. For nitrogen fixation, it appears that neither soil nor bacteria are absolutely necessary, what really seems indispensable is a suitable solid surface where water, oxygen, nitrogen and an energy material are properly adsorbed and are in intimate contact, so that the slow oxidation of the energy material leading to liberation of energy and subsequent nitrogen fixation can be possible.

Summary

Careful experiments carried on show that marked nitrogen fixation can take place when organic substances undergo slow oxidation on chemically pure metallic oxides as surfaces both under sterile and unsterile sets of experiments. Our experiments clearly establish that for fixation of atmospheric nitrogen, neither soil nor microorganisms are necessary. What really seems indispensable is a suitable solid surface where water, oxygen, nitrogen and an energy material are properly adsorbed and are in intimate contact, so that the slow oxidation of the energy material leading to liberation of energy and subsequent fixation of nitrogen is possible.

Moreover nitrogen fixation is associated with loss of nitrogen in the elementary state due to the formation and decomposition of the unstable explosive substance NH_4NO_2 which breaks up as in the equation,

$$NH_4NO_2 = N_2 + 2H_2O + 718 \text{ K. cal.}$$
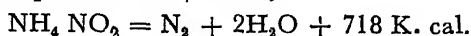
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Effect of fairly high doses of nitrogenous fertilizers on the amount of compost produced during the decomposition of incubated Kans, Wheat Straw, Paddy Straw, Screened Municipal Rubbish

By

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Introduction

The fundamental principle involved in the composting of organic substances having C/N ratio greater than 10 to humus with a C/N of 10 is to supply an adequate amount of minerals, *e.g.*, available nitrogen, phosphate, potash, lime, iron and air etc. for the growth of micro-organisms which can utilize the energy materials present in the composting matter. The raw material to be composed has usually a C/N ratio much greater than 10. The micro-organisms are believed to destroy the energy material and obtain energy and carbohydrate for building up their body materials. The aim of composting is to decrease the amounts of carbohydrates and save the nitrogenous substances and obtain a material relatively richer in nitrogen and poorer in carbon.

Albrecht[1] used 45 lbs of ammonium sulphate, 15 lbs of superphosphate and 40 lbs of finely ground lime-stone in the composting of straw. He recommended 150 lbs of this material mixture per ton of straw to be composted. In Rothamsted 3·5 parts of ammonium sulphate were added for 100 lbs of straw in the Adco process. It was observed that at first the nitrogen was first assimilated by micro-organisms and the dry matter lost to the extent of 20% of the dry weight of the straw. The decomposition then slowed down and went on till 50% loss of the dry matter. Martin and Wang[2] have determined the loss during composting of different organic substances.

Recently, Pinck, Allison and Gaddy[3] added different weights of urea to 12·5 tons of mature millet residues per acre on loamy sand and obtained the following results :

Nitrogen added lbs/acre	Gain in carbon tons/acre	Gain in nitrogen lbs/acre
0	1·25	171
200	1·82	276
400	2·20	300
800	2·89	402

In order to throw further light on the amounts of composts obtained at different doses of nitrogenous fertilizers, we have carried out a very large number of experiments on the composting of Kans, wheat straw, paddy straw and screened municipal rubbish using different doses of ammonium sulphate and urea. The results obtained are recorded in the following tables.

[491]

TABLE 1

Analysis of organic materials (oven dried)

Constituents	Kans	Wheat straw	Paddy straw	Screened Municipal rubbish
Loss on ignition%	91·5124	91·1600	86·7700	37·82
Ash %	8·4876	8·8400	13·23	62·18
HCl insoluble %	4·6839	5·3875	4·6700	49·97
Sesquioxide %	0·8740	1·4321	2·6234	8·2104
Fe_2O_3 %	0·3854	0·6015	1·1573	3·9753
CaO %	0·7726	0·7439	2·6854	1·8693
P_2O_5%	0·5283	0·5432	0·3857	0·8624
K_2O %	0·8975	1·5793	1·5346	0·7905
MgO %	0·6827	0·1510	0·1163	0·3857
Carbon	39·6462	36·700	31·5100	19·5200
Nitrogen	0·6819	0·6015	0·4900	0·6583
C/N ratio	58·1	61·00	64·2	29·6

Sources of nitrogen	Nitrogen %
Ammonium sulphate	21·1
Urea	45·7

TABLE 2

100 gms Kans + 40% moisture   *Incubation Temp. 36°C*

Period of exposure in days	Carbon (gms)	Nitrogen (gms)	Nitrogen increase (+) or decrease (−) (gms)	Carbon oxidised (gms)	Weight of compost produced (gms)	Percentage loss in weight	C/N ratio
0	39·6462	0·6817	—	—	100	—	58·1
50	30·7655	0·8554	+0·1737	8·8807	91·30	8·7	35·9
100	25·0960	0·9557	+0·2740	14·5502	85·73	14·27	26·2
150	20·3781	0·8945	−0·0612	19·2681	80·96	19·04	22·7

TABLE 3

100 gms wheat straw + 40% moisture

0	36·7000	0·6015	—	—	100	—	61·0
50	28·7252	0·7638	+0·1623	7·9748	92·20	7·80	37·6
100	22·9417	0·8657	+0·2642	13·7583	86·51	13·49	26·4
150	18·3741	0·8168	−0·0489	18·3259	81·70	18·30	22·4

TABLE 4

100 gms paddy straw + 40% moisture

0	31·5000	0·4900	—	—	100	—	64·2
50	24·1592	0·6408	+0·1508	7·3408	92·81	7·19	37·7
100	19·2148	0·7464	+0·2564	12·2852	87·97	12·03	25·7
150	14·8261	0·7007	−0·0457	16·6739	83·59	16·41	21·1

TABLE 5

100 gms Municipal rubbish + 40% moisture Incubation Temp. 36°C

Period of exposure in days	Carbon (gms)	Nitrogen (gms)	Nitrogen increase (+) or decrease (−) (gms)	Carbon oxidised (gms)	Weight of compost produced (gms)	Percentage loss in weight	C/N ratio
0	38·5400	0·8215	—	—	100	—	46·7
50	29·4974	0·9967	+0·1752	9·026	91·14	8·86	29·6
100	23·5565	0·0940	+0·2725	14·9835	85·30	14·70	21·5
150	19·0183	0·0377	−0·0563	19·5217	80·48	19·52	18·2

TABLE 6

100 gms Kans + 1 gm N as Ammonium sulphate

0	39·6462	1·6817	—	—	104·74	—	23·5
50	28·3878	1·7449	+0·1032	11·2584	94·19	10·00	16·2
100	21·2127	1·5831	−0·2018	18·4355	86·10	17·5	13·3
150	15·6207	1·4307	−0·2142	24·0255	80·40	23·2	10·9

TTBLE 7

100 gms Kans + 1 gm N as urea

0	39·6462	1·6817	—	—	102·20	—	23·5
50	28·6055	1·7864	+0·1047	11·0407	91·26	10·7	16·0
100	21·3969	1·5778	−0·2086	18·2493	86·75	18·1	13·5
150	15·7710	1·4692	−0·3172	23·8752	78·01	23·7	10·7

TABLE 8

100 gms wheat straw + 1 gm N as Ammonium sulphate

0	36·7000	1·6015	—	—	104·74	—	22·8
50	26·4316	1·7119	+0·1104	10·2684	94·58	9·8	15·4
100	19·7248	1·5107	−0·2012	16·9752	87·56	16·4	12·3
150	14·1216	1·4027	−0·3092	22·5784	82·47	21·3	10·0

TABLE 9

100 gms wheat straw + 1 gm N as urea

0	26·7000	1·6015	—	—	102·20	—	22·8
50	26·6244	1·7140	+0·1125	10·0756	92·23	9·8	14·9
100	20·2717	1·5092	−0·2048	16·4283	85·77	16·2	13·4
150	14·4164	1·4017	−0·3123	22·2836	79·92	21·8	10·2

TABLE 10

100 gms Paddy straw + 1 gm N as Ammonium sulphate

0	31·500	1·4900	—	—	104·74	—	21·1
50	22·1736	1·5963	+0·1063	9·3264	95·52	8·7	13·9
100	15·9654	1·4018	−0·1945	15·5346	89·01	15·0	11·3
150	10·8765	1·2970	−0·2993	20·6235	83·82	19·0	8·3

TABLE 11

100 gms Paddy straw + 1 gm N as urea   Incubation Temp. 36°C

Period of exposure in days	Carbon (gms)	Nitrogen (gms)	Nitrogen increase (+) or decrease (−) (gms)	Carbon oxidised (gms,	Weight of compost produced (gms)	Percentage loss in weight	C/N ratio
0	31·500	1·4900	−	−	102·20	−	21·1
50	22·3522	1·5936	+0·1036	9·1478	92·56	9·4	14·0
100	16·1935	1·3953	−0·1983	15·3065	86·89	14·9	11·6
150	11·1518	1·2909	−0·3027	20·3482	81·85	19·9	8·6

TABLE 12

100 gms Municipal rubbish + 1 gm N as Ammonium sulphate

0	19·5200	1·6583	−	−	104·74	−	11·7
50	11·2315	1·5073	+0·1510	8·2885	96·45	8·5	7·4
100	7·3516	1·4263	−0·2320	12·1684	92·54	11·7	5·1
150	4·3082	1·3562	−0·3021	15·2118	89·53	14·5	3·1

TABLE 13

100 gms Municipal rubbish + 1 gm N as urea

0	19·5200	1·6583	−	−	102·20	−	11·7
50	11·5436	1·5033	+0·1550	7·9763	94·22	7·8	7·6
100	7·7532	1·4131	−0·2444	11·7608	90·43	11·5	5·4
150	4·5486	1·2956	−0·3627	14·9714	87·23	14·1	3·5

TABLE 14

100 gms Kans + 1·5 gms N as Ammonium sulphate

0	39·6462	2·1817	−	−	107·11	−	18·9
50	29·5219	2·0734	−0·1083	10·1243	96·88	9·5	14·2
100	22·4212	1·8360	−0·3457	17·2246	89·41	16·4	12·2
150	17·1078	1·6645	−0·5172	22·5384	80·06	22·6	10·2

TABLE 15

100 gms Kans + 1·5 gms N as urea

0	39·6462	2·1817	−	−	103·30	−	18·1
50	29·6378	2·0683	−0·1134	10·0084	93·18	9·8	14·3
100	22·7769	1·8303	−0·3514	16·8693	86·08	15·7	12·4
150	17·4723	1·6508	−0·5309	22·1739	80·60	22·1	10·5

TABLE 16

100 gms wheat straw + 1·5 gms N as Ammonium salphate

0	36·7000	2·1015	−	−	107·11	−	14·4
50	26·9462	2·0032	−0·0983	9·7538	97·27	9·1	13·4
100	21·2704	1·7963	−0·3052	15·4295	91·38	14·5	11·8
150	15·2792	1·6057	−0·4958	21·4208	86·20	19·5	9·5

TABLE 17

100 gms wheat straw + 1·5 gms N as urea   Incubation Temp. 36°C

Period of exposure in days	Carbon (gms)	Nitrogen (gms)	Nitrogen increase (+) or decrease (−) (gms)	Carbon oxidised (gms)	Weight of compost produced (gms)	Percentage loss in weight	C/N ratio
0	36·7000	2·1015	−	−	103·00	−	17·4
50	27·2716	1·9984	− 0·1031	9·4283	93·77	9·2	13·6
100	21·6608	1·7893	− 0·3122	15·0392	87·96	14·8	12·1
150	15·6582	1·5987	− 0·5028	21·0418	87·76	20·8	9·8

TABLE 18

100 gms Paddy straw + 1·5 gms N as Ammonium sulphate

0	31·5000	1·9900	−	−	107·11	−	15·8
50	23·2504	1·8832	− 0·1068	8·2436	98·98	7·6	12·3
100	17·0261	1·7826	− 0·2506	14·4739	92·39	13·7	9·5
150	12·1737	1·6490	− 0·3842	19·3263	87·40	18·4	7·3

TABLE 19

100 gms Paddy straw + 1·5 gms N as urea

0	31·5000	1·9900	−	−	103·30	−	15·8
50	23·4848	1·8264	− 0·1636	8·0125	95·32	7·7	12·8
100	17·3658	1·7651	− 0·2614	14·1342	88·92	13·9	9·8
150	13·6525	1·5908	− 0·3992	18·8475	84·05	18·6	8·7

TABLE 20

100 gms Municipal rubbish + 1·5 gms N as Ammonium sulphate

0	19·5200	2·1583	−	−	107·11	−	9·0
50	12·5314	1·9034	− 0·2549	6·9886	100·12	6·5	6·5
100	8·3462	1·7508	− 0·4075	11·1738	95·94	10·4	4·7
150	5·6382	1·6014	− 0·5569	13·8818	93·23	12·9	3·5

TABLE 21

100 gms Municipal rubbish + 1·5 N as urea

0	19·5200	2·1583	−	−	103·30	−	9·0
50	12·6608	1·9002	− 0·2581	6·8592	96·44	6·6	6·6
100	8·5262	1·7463	− 0·4110	10·9938	92·31	10·6	4·8
150	5·8204	1·5983	− 0·5600	13·6996	89·60	13·2	3·0

Experimental

100 gms of each material, powdered, sieved and dried at 105°C for 5 to 6 hours, were taken in glass bottles. To some of these bottles, different nitrogenous fertilizers containing one gram of nitrogen were added while to the other bottles 1·5 gms. of nitrogen from different sources were added.

After a definite interval of time, composts were weighed and samples were taken out for analysis.

Discussion

In these experiments on composting lasting for 15 days the maximum loss in weight was 23·7 % with 100 gms Kans to which one gram of nitrogen was added as ammonium sulphate, with 1 gram of nitrogen as urea the loss is 22·2%. While using 1·5 gms of nitrogen. The loss with ammonium sulphate is 22·3% and with urea 22·1 % against a loss of 19·04% without any nitrogenous fertilizer.

With wheat straw at the rate of 1 gram nitrogen, the loss with ammonium sulphate is 21·3% and with urea 21·8% with 1·5 gms of nitrogen and wheat straw the losses are 19·5% with ammonium sulphate and 20·8% with urea.

More or less similar results have been obtained with the organic substances, showing a slight decrease in the loss with a higher dose of other nitrogenous fertilizers. But, the loss of solid matter without adding nitrogenous fertilizer is always smaller than in the presence of nitrogenous fertilizers. The carbon nitrogen ratios show that these values are smaller in the presence of nitrogenous fertilizers.

Moreover, the total nitrogen estimations prove that without nitrogenous fertilizers there is appreciable nitrogen fixation in the composting of plant materials, but, in the presence of nitrogenous fertilizers, there is marked loss of nitrogen in the system. The results obtained by American workers show that there is gain in nitrogen in the composting of millet residues without the addition of urea. But, when heavy doses of nitrogen in the form of urea are added, the greater part of the added nitrogen is lost. Hence, it appears that adding large doses of nitrogenous fertilizers involves heavy loss of nitrogen added and the amount of compost obtained is smaller than the compost obtained in the absence of nitrogenous fertilizers. But, the percentage of nitrogen present in the compost obtained by adding nitrogenous fertilizers in organic matter, is greater than in the absence of nitrogenous fertilizer and the nitrogenated compost should be able to produce better crops.

Investigators in Newzealand found that the most rapid composting was achieved with a C/N ratio of about 26. Moreover, their nitrogen losses, when composting the materials with initial C/N ratios of 22 to 29, were around 50%. Scott reported nitrogen losses up to 60% in some of his experiments. Nitrogen losses of around 50% were observed in the University of California. Waksman found that in manure composts, the nitrogen was conserved only when the C/N ratio was adequate and when immediate decomposition set in. Russell[4] has reported a loss of 51% nitrogen at 35°C when straw is composted for 64 days with ammonium carbonate. Bould[5] observed losses of nitrogen from 28 to 43% in composting.

The loss of nitrogen from composts is usually associated with the total nitrogen content of the materials to be composted and with the temperature rise of the system in composting. The higher the nitrogen content of the system and higher the temperature attained by the system, the greater the loss of nitrogen.

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Influence of light and phosphates on Carbon-Nitrogen changes and mineralization of Nitrogen during the decomposition of Municipal Rubbish

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Introduction

There is an intimate relationship between sanitation and Agriculture in all parts of the world. In agricultural areas the utilization of human and animal wastes is of great importance from both the public health and the agricultural point of view.

The disposal and utilization of city wastes is also becoming very important in highly industrialized areas because of (*a*) the ever increasing difficulties in disposing of great accumulations of wastes from cities in a sanitary and orderly manner, (*b*) the ever increasing threat to soil fertility due to the great decrease in the amount of animal manure ; and (*c*) the ever increasing and intensive demands being put on the agricultural lands to produce more food.

Approximately one fourth of the food and fibre produced in the world is wasted as municipal garbage and waste. Taking the world production of food and fibre at 1800 million tons, the municipal waste and garbage comes to 450 million tons containing not less than 9 to 10 million tons of nitrogen. Moreover, the garbage and waste contains valuable amounts of potash, phosphate, trace elements and carbonaceous compounds which, under favourable conditions, can fix atmospheric nitrogen, specially when phosphated with basic slag or rock phosphate. It appears, therefore, that this waste, if properly preserved and handled, and managed for nitrogen fixation, can supply 15 to 18 million tons of nitrogen, 7 to 8 million tons of phosphate and about 15 to 20 million tons of potash.

Because of the increasing world population all lands have to produce more and more food. World research has definitely demonstrated that this demand on increased food production cannot be met by artificial fertilizers, which in long run, decrease the humus capital of land. Hence, countries like Holland, Belgium and Germany, which are densely populated are producing large amounts of compost and other organic humus producing materials. On the other hand, in countries like China, India and other eastern parts of the world, where there is still greater population pressure and food demands and small amounts of artificial fertilizers are used, this humus supply must increase enormously and all organic matter should be converted into phosphated humus.

Hence, in view of the importance of municipal waste in building up the land fertility permanently and in increasing the food production, the present experiments were undertaken to determine the effect of rock phosphate, superphosphate and basic (Thomas) Slag on the nitrogen transformations in decomposing waste.

Experimental

Under the action of solar light

20 Kilograms of municipal waste were taken in each box of Jamun (Jambu, wood of smooth surface which is little affected by water. The joints at the corners and bottom of the boxes were cemented with plaster of Paris. The ratio of length, breadth and depth was practically the same as advocated by Howard and Vad (1933) in their composting experiments.

The dimension of the boxes was $30'' \times 15'' \times 6''$. Superphosphate, basic slag, and rock phosphate were added at the rate of 0.5% P_2O_5. The mass was stirred thrice in a week and 40% moisture was maintained throughout the period of experiment. One set was exposed to sunlight, while the other was kept in the laboratory.

After a definite period of time, the whole of the material of each box was weighed and then a known weight of the samples was taken out for analysis. The samples were powdered and passed through a 60 mesh sieve and analysed on oven dry basis.

TABLE 1

Analysis of Municipal Rubbish used in boxes (ovendried)

Loss on ignition %	35·73
Ash %	64·27
HCl insoluble (Silica) %	52·38
Sesquioxide %	7·83
Fe_2O_3 %	3·52
CaO %	1·7426
P_2O_5 %	0·8196
K_2O %	0·7305
MgO	0·3213
Carbon %	15·3
Nitrogen %	0·6204
NH_3–N %	0·0132
NO_3–N %	0·0203
Percentage of available N/Total N	5·4
Available P_2O_5 %	0·1263
pH (1 : 5)	8·2
Conductivity $\times$ 10^{-3} mhos/cm	1·6
C/N ratio	24·6

TABLE 2

20 Kgs. Municipal rubbish + 40% Moisture (control)   *Av. Temp. 38°C*

Period of exposure in days	Total carbon (gms)	Total nitrogen (gms)	NH_3—N (gm)	NO_2—N (gm)	Total available N/ total N %	Nitrogen increase (+) or decrease (−)(gms)	Available P_2O_5 %	C/N ratio
				Sunlight				
0	3060·0	124·08	2·6400	4·0600	5·4	—	0·12·63	24·6
45	2463·3	152·37	5 6214	7·4824	8·6	+28·29	0·1475	16·1
90	1852·9	208·79	10·2416	16·0750	12·5	+84·71	0·1654	8·8
120	1609·6	193·39	8·4352	12·2245	15·2	−15·4	0·1839	8·3
				Undershade				
0	3060·0	124·08	2·6400	4·0600	5·4	—	0·1263	24·6
45	2542·9	145·65	4·3752	6·2572	7·3	+21·59	0·1337	17·5
90	31·0·6	179·88	7·8422	11·4050	10·7	+55·80	0·1525	11·7
120	1799·3	165·99	6·2475	9·5216	9·5	−13·89	0·1635	10·8

TABLE 3

20 Kgs. Municipal rubbish + 0·5% P_2O_5 as T.R.P. + 40% moisture

Period	Total carbon	Total nitrogen	NH_3—N	NO_2—N	Avail N %	N increase/decrease	P_2O_5 %	C/N
				Sunlight				
0	3060·0	124·08	2·6400	4·0600	5·4	—	0·1263	24·6
45	2252·0	170·24	7·9824	10·0630	10·6	+46·16	0·2145	13·2
90	1661·0	248·65	16·5827	24·2959	16·4	+124·57	0·2692	6·6
120	1306·0	222·55	12·5436	19·2810	14·3	−26·10	0·2783	5·8
				Undershade				
0	3060·0	124·08	2·6400	4·0600	5·4	—	0·1263	24·6
45	2310·0	160·44	6·3821	8·3784	9·2	+36·36	0·1752	14·3
90	1909·0	201·51	10·2490	15·7553	13·4	+77·43	0·2096	9·4
120	1545·0	184·38	8·5724	13·5532	12·0	−17·13	0·2372	8·3

TABLE 4

20 Kgs Municipal rubbish + 0·5% P_2O_5 as T.B.S. + 40% moisture

Period	Total carbon	Total nitrogen	NH_3—N	NO_2—N	Avail N %	N increase/decrease	P_2O_5 %	C/N
				Sunlight				
0	3060·0	124·08	2·6400	4·0600	5·4	—	0·1263	24·6
45	2148·0	173·96	8·4705	13·4224	22·7	+49·88	0·2564	12·3
90	1539·0	255·11	18·5084	31·4933	19·6	+131·03	0 2829	6·0
120	1239·0	223·72	14·5463	23·9335	17·2	−31·39	0·3012	5·5
				Undershade				
0	3060·0	124·08	2·6400	4·0600	5·4	—	0·1263	24·6
45	2283·0	162·17	6·0634	9·8093	9·8	+38·09	0·1903	14·0
90	1857·0	204 25	11·0842	18·12·6	14·3	+80·17	0·2?78	9·9
120	1487·0	184·64	9·5824	15·1594	13·4	−19·61	0·2624	8·0

TABLE 5

Av. Temp. 38°C

20 *Kgs Municipal rubbish* + 0·5% P_2O_5 *as K.B.S.* + 40% *moisture*

Period of exposure in days	Total carbon (gms)	Total nitrogen (gms)	NH_3—N (gm)	NO_3—N (gm)	Total available N/ total N %	Nitrogen increase (+) or decrease (−) (gms)	Available P_2O_5 %	C/N ratio
Sunlight								
0	3060·0	124·08	2·6400	4·0600	5·4	−	0·1263	24·6
45	2178·0	172·10	8·2403	11·5512	11·5	+48·02	0·2438	12·6
90	1578·0	252·38	16·7284	27·2029	18·2	+128·29	0·2785	6·2
120	1291·0	222·85	13·0837	23·2408	16·3	− 29·53	0·2972	5·7
Undershade								
0	3060·0	124·08	2·6400	4·0600	5·4	−	0·1263	24·6
45	2434·0	160·69	5·6708	9·0667	9·2	+36·11	0·1903	15·1
90	1829·0	201·76	10·5406	16·8988	13·6	+77·68	0·2368	9·0
120	1521·0	184·92	9·0437	14·4411	12·7	− 16·84	0·2564	8·2

TABLE 6

20 *Kgs Municipal rubbish* + 0·5% P_2O_5 *as A.R.P.* (C) + 40% *moisture*

Period of exposure in days	Total carbon (gms)	Total nitrogen (gms)	NH_3—N (gm)	NO_3—N (gm)	Total available N/ total N %	Nitrogen increase (+) or decrease (−) (gms)	Available P_2O_5 %	C/N ratio
Sunlight								
0	3060·0	124·08	2·6400	4·0600	5·4	−	0·1263	24·6
45	2224·0	171·36	7·0584	12·2053	11·3	+47·28	0·2197	12·9
90	1637·0	249·16	15·8273	28·5232	17·8	+125·08	0·2718	6·5
120	1296·0	222·74	12·7478	22·5541	15·4	− 26·42	0·2814	5·8
Undershade								
0	3060·0	124·08	2·6400	4·0600	5·4	−	0·1263	24·6
45	2305·0	163·32	6·1342	8·5646	9·0	+39·24	0·1824	14·1
90	1878·0	202·15	10·2759	15·4079	13·2	+78·07	0·2153	9·2
120	1534·0	183·42	8·4372	13·5732	12·0	− 19·73	0·2437	8·3

TABLE 7

20 *Kgs Municipal rubbish* + 0·5% P_2O_5 *as B.B.S.* + 40% *moisture*

Period of exposure in days	Total carbon (gms)	Total nitrogen (gms)	NH_3—N (gm)	NO_3—N (gm)	Total available N/ total N %	Nitrogen increase (+) or decrease (−) (gms)	Available P_2O_5 %	C/N ratio
Sunlight								
0	3060·0	124·08	2·6400	4·0600	5·4	−	0·1263	24·6
45	2140·0	175·72	9·3257	13·8693	13·2	+51·64	0·2608	12·1
90	1530·0	259·90	20·3798	34·7192	21·2	+135·82	0·2894	5·8
120	1233·0	227·57	15·4142	26·6863	18·5	− 32·33	0·3173	5·4
Undershade								
0	3060·0	124·08	2·6400	4·0600	5·4	−	0·1763	24·6
45	2276·0	163·57	6·5237	10·4776	10·4	+39·49	0·2004	13·9
90	1850·0	205·62	12·4628	18·1774	14·9	+81·54	0·2417	8·9
120	1478·0	185·35	10·1874	15·0202	13·6	− 20·27	0·2683	7·9

TABLE 8

Av. Temp. 38°C

20 Kgs Municipal rubbish + 0·5% P₂O₅ as superphosphate + 40% moisture

Period of exposure in days	Total carbon (gms)	Total nitrogen (gms)	NH₃—N (gm)	NO₃—N (gm)	Total available N/ total N %	Nitrogen increase (+) or decrease (−) (gms)	Available P₂O₅ %	C/N ratio
				Sunlight				
0	3060·0	124·08	2·6400	4·0600	5·4	—	0·1263	24·6
45	2240·0	170·74	7·0439	11·3960	10·8	+44·66	0·2564	13·1
90	1612·0	249·15	16·4326	27·1787	17·5	+125·07	0·2893	6·4
120	1540·0	221·50	12·3284	18·0171	15·7	−27·65	0·2957	6·0
				Undershade				
0	3060·0	124·08	2·6400	4·0600	5·4	—	0·1263	24·6
45	2350·0	157·95	5·1246	8·1432	8·4	+33·87	0·2337	14·8
90	1858·0	200·39	8·9683	16·1816	12·8	+76·31	0·2578	9·2
120	1576·0	182·15	7·4326	12·6039	11·0	−18·24	0·2718	8·6

TABLE 9

20 Kgs Municipal rubbish + 0·5% P₂O₅ as B.R.P. + 40% moisture

Period	Total carbon (gms)	Total nitrogen (gms)	NH₃—N (gm)	NO₃—N (gm)	Total available N/ total N %	Nitrogen increase (+) or decrease (−) (gms)	Available P₂O₅ %	C/N ratio
				Sunlight				
0	3060·0	124·08	2·6400	4·0600	5·4	—	0·1263	24·6
45	2310·0	169·12	7·3652	10·2233	10·4	+45·04	0·2309	13·6
90	1692·0	246·30	14·3754	24·0494	15·6	+122·22	0·2654	6·8
120	1420·0	220·50	12·3475	17·1995	13·4	−25·80	0·2873	6·4
				Undershade				
0	3060·0	124·08	2·6400	4·0600	5·4	—	0·1263	24·6
45	2442·0	151·95	5·0752	7·8406	8·5	+27·87	0·1827	16·0
90	1949·0	196·67	8·7246	14·8591	12·5	+72·59	0·2214	9·9
120	1737·0	178·96	7·4653	13·3818	11·7	−17·71	0·2384	9·7

Discussion

A perusal of the foregoing results reveals that there is a considerable oxidation of carbonaceous compounds in municipal rubbish and also an increase in the nitrogen content of the system, when it is allowed to undergo oxidation in air at ordinary temperature. But, when the system is illuminated by artificial or solar light, the velocity of the oxidation of the carbonaceous compounds is greatly enhanced. Moreover, when phosphates were incorporated with municipal rubbish in presence of light, there was greater oxidation of the carbonaceous compounds. But the carbon oxidation with different phosphates was different, when the dose of the phosphate was the same. They are as follows (vide Table 2–9).

Original Carbon content of the system 3060·0 gms

	Treatments		Oxidation of carbon (gms		
			Days	Light	Dark
(i)	Municipal Rubbish alone		90	1207·7	939·4
(ii)	do	+ Trichinopoly rock phosphate	90	1399·0	1151·0
(iii)	do	+ Tata basic slag	90	1521·0	1203·0
(iv)	do	+ Kulti Basic slag	90	1482·0	1231·0
(v)	do	+ Algerian rock phosphate "C"	90	1423·0	1182·0
(vi)	do	+ Belgian basic slag	90	1530·0	1210·0
(vii)	do	+ Superphosphate	90	1448·0	1202·0
(viii)	do	+ Bihar rock phosphate	90	1368·0	1 11·0

From the foregoing results it is clear that the oxidation of carbon of the system to which phosphate was added and which was exposed to light, is always higher than that of the covered one.

It is also observed that there is an increase of the nitrogen in the system, but the fixation of the nitrogen is greatly enhanced when incorporated with phosphate and is exposed to the light as is evident from the following results (vide table 2-9).

Gain in nitrogen
Original nitrogen 1224·1 gms

	Treatments		Gain in nitrogen (gm)		
			Days	Light	Dark
(i)	Municipal rubbish alone		90	84·71	55·80
(ii)	do	+ T. R. P.	90	124·37	77·43
(iii)	do	+ T. B. S.	90	131·03	80·17
(iv)	do	+ K. B. S.	90	128·29	77·68
(v)	do	+ A. R. P. "C"	90	125·08	78·07
(vi)	do	+ B. B. S.	90	135·82	81·54
(vii)	do	+ Superphosphate	90	125·07	76·31
(viii)	do	+ B. R. P.	90	122·22	72·59

It is clear from the above results that during the decomposition and partial oxidation of municipal rubbish in boxes, there is an appreciable amount of nitrogen fixation. The gain in nitrogen on composting with phosphate has been significant.

The increase of nitrogen during the decomposition and oxidation has been reported by a number of workers. Gotaas and coworkers[1] reported nitrogen fixation in the composting of refuse having a C/N rato lower than 30. Gaur[2] and Gulab Singh[3] have reported appreciable nitrogen fixation in the composting of carbonaceous compounds. Acharya and coworkers[4] have found that addition of earth in decomposing refuse helps in the conservation and fixation of nitrogen,

Moreover, throughout our experiments on the decomposition of municipal rubbish we have observed that the availability of phosphate has greatly increased during the period of composting as is clear from the following results.

Available P_2O_5

Original available $P_2O_5 = 0.1263\%$

Treatments		Days	Available $P_2O_5\%$	
			Light	Dark
1. Municipal rubbish alone		120	0.1839	0.1635
2. do	+ T. R. P.	120	0.2783	0.2372
3. do	+ T. B. S.	120	0.3012	0.2624
4. do	+ K. B. S.	120	0.2972	0.2564
5. do	+ A. R. P.	120	0.2814	0.2437
6. do	+ B. B. S.	120	0.3173	0.2683
7. do	+ S. P.	120	0.2957	0.2718
8. do	+ B. R. P.	120	0.2873	0.2384

This increased availability of P_2O_5 is due to the fact that the tricalcium phosphate, which is present in rock phosphates and basic slags, is converted into more soluble forms of phosphate such as dicalcium and monocalcium phosphate by the action of carbonic acid and the other acids produced during the oxidation and decomposition of the organic substances. This is clear from the following results :

$$(i) \quad Ca_3(PO_4)_2 + CO_2 + H_2O = 2CaHPO_4 + CaCO_3$$
$$(ii) \quad Ca_3(PO_4)_2 + 2CO_2 + 2H_2O = Ca(HPO_4)_2 + 2CaCO_3$$
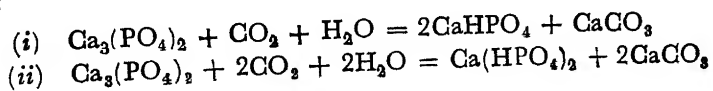
The following observation of Dhar[5] is of great interest in this connection :

"The third dissociation constant of phosphoric acid is smaller than the first and second dissociation constants of carbonic acid and, hence, carbonic acid converts tricalcium phosphate into dicalcium phosphate which is always more soluble than tricalcium phosphate. Thus the availability of phosphate is increased in the soil rich in carbonic acid obtained from the oxidation of organic substances similarly nitrous and nitric acids formed in the soil from ammonification and nitrification of proteins, make phosphate more readily available. Thus phosphates are more useful in presence of organic substances like farmyard manure, straw, etc. undergoing slow oxidation".

Moreover, increase in the availability of nitrogen has also been observed throughout our experiments as is evident from the following results :

Available nitrogen
Original available nitrogen over total nitrogen 5·4%

Treatments		Days	Available nitrogen over total nitrogen%	
			Light	Dark
1. Municipal rubbish alone		90	12·5	10·7
2. do	+ T. R. P.	90	16·4	13·4
3. do	+ T. B. S.	90	19·6	14·3
4. do	+ K. B. S.	90	18·2	13·6
5. do	+ A. R. P. "C"	90	17·8	13·2
6. do	+ B. B. S.	90	21·2	14·9
7. do	+ S. P.	90	17·5	12·8
8. do	+ B. R. P.	90	15·6	12·5

The above experimental results prove that the availability of nitrogen is always higher in the phosphated and the exposed system than in the covered ones.

In our composting experiments it is observed that after certain interval of time, there is loss of nitrogen. The reason for this loss can be explained on the basis of ammonium nitrite formed during the nitrification and nitrous compounds or proteins present in the system. Ammonium nitrite is a very unstable substance and gets decomposed as nitrogen gas.

We have also determined the pH and conductivity of the system after definite intervals of time. Upto a certain time the pH of the exposed composts is lower than that of the covered ones or kept under shade but, as soon as the breakdown of acids and mineralization begins, the exposed experiment showed the pH values more on the alkaline side than the covered ones. In the beginning, the conductivity of the exposed set is much greater than that of covered set, but, later on, this difference in the conductivity decreased.

From these experiments we conclude that phosphates are useful in acelerating the fixation of atmospheric nitrogen and are also helpful in the mineralization of the nitrogenous compounds.

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Studies on the effect of phosphates and Kans on nitrogen loss during the decomposition and nitrification of oil cakes

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Introduction

Animal and plant materials like blood, fish, bonemeal, tankage wool residue, meat residue, guano, human extreta, oil cakes, boot, garbage etc., have been used as manure from ancient times. But, the chemical changes involved in their action have been cleared up only in recent years. When they are mixed with soil the oxidation of organic compounds takes place with liberation of carbon dioxide and ammonia, which in turn is further oxidised to nitrite and nitrate. But, a good deal of fertilizing value is wasted away as nitrogen gas escapes without any benefit either to the crop on the soil.

Researches of Lipman and Blair[1], Russell and Richards[2] and Shutt[3] as well as others show that nitrogen in the gaseous state is lost from soils when the conditions are favourable for oxidation. The losses of nitrogen in the process may be double than that of the amount of nitrogen taken up by plants grown on the same soil. Nearly 70 % of the added nitrogen is said to be lost when wheat plots in Rothamsted have annually received 14 tons of farm yard manure containing 200 lbs of nitrogen per acre.

Russell[4] has stated this problem of the loss of nitrogen in the following words : ''There is considerable difficulty in accounting for the nitrogen lost from the soil during the first 20–30 years of cultivation. It has, therefore, been supposed that nitrogen is evolved during the oxidation and, as all attempts to break nitrogen from NO_3 in these conditions have failed, it is assumed to come from the organic matter. This assumption evolved the difficulty that no loss has been observed in the straight forward bacterial oxidation of organic substances such as albumin, asparagin or mixtures such as urine or faeces. Yet, somehow and somewhere gaseous nitrogen must be evolved to balance the considerable amount of fixation that is known to take place''. Barrit[5] thought that nitrogen may be lost as a result of chemical reaction between nitrite and amines under acid conditions according to the following equation :

$$RNH_2 + HNO_2 = ROH + N_2 + H_2O$$
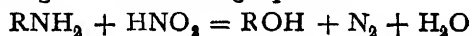
Several years ago Dhar, Tandon and Mukherji[6] showed that the loss of nitrogen on exposing ammonium salt solutions to light and air is always greater in light than in the dark and they have also made a systematic study of the process of ammonification and nitrification. They observed that bacterial theory of nitrification has been over-emphasised. They have reported that ammonification or nitrification can be a photo-chemical phenomenon.

The loss of nitrogen in composting is usually associated with the total nitrogen content of the materials to be composted and the temperature, aeration and light absorption.

We have studied systematically the loss of nitrogen from oil cakes in their nitrification. Moreover, we have tried to investigate the effect of the organic matter KANS – reinforced with different phosphates in checking the loss of nitrogen during the decomposition of oil cakes.

Experimental

50 gms of powdered oil cakes dried at 105°C and passed through a 60 mesh sieve were taken in wide mouthed bottles of equal size and phosphate was added to the extent of 0·5% P_2O_5. 50 gms of well dried, 60 mesh sieved KANS was mixed well with 50 gms of oil cakes. One set was exposed to the light of a 100 W. electric bulb. Another set was kept covered with a thick piece of black cloth to exclude the light. Moisture level was maintained at 40% and stirred thrice in a fortnight. At certain intervals of time samples were taken and analysed for total carbon, total nitrogen, ammoniacal nitrogen and nitric nitrogen.

TABLE 1

Analysis of oil cakes (over dried) and Kans

	Neem cake (Azadirachta Indica)	Ground nut cake (Arachis hypoaea)	Castor cake (Recinus communis	Kans (Saccharam spontaneum
Loss on ignition %	92·17	92·25	90·83	91·5124
Ash %	7·83	7·75	9·17	8·4876
HCl insoluble %	1·0613	2·0800	2·85	4·6839
Sesquioxide %	0·4032	0·5373	0·4413	0·8740
Fe_2O_3 %	0·1562	0·2504	0·,513	0·?253
Total P_2O_5%	0·1572	0·2083	0 2016	0·5283
Total K_2O %	0·9273	3·0754	3·3273	0· 975
Total CaO %	1·6124	1·4162	1·6584	0·7726
Total MgO %	0·6056	0·4512	0·6848	0·6827
Total carbon %	45·36	39·40	43 08	39·6462
Total nitrogan %	7·9368	5·7846	4·7890	0·6817
C/N ratio	5·7	6 8	8·9	59·1

Sources of Phosphate P_2O_5%   2. Belgian Basic Slag   17·82
1. Tata Basic Slag   7·57   3. Superphosphate   16·52

TABLE 2

100 gms *Neem Cake* + 40% *moisture (control)*   Av. Temp. 36°C

Period of exposure in days	Total carbon (gms)	Total nitrogen (gms)	NH_3—N (gm)	NO_3—N (gm)	Nitrogen increase (+) or decrease(−)(gms)	Carbon oxidised (gms)	C/N ratio
			Light				
0	45·36	7·9368	—	—	—	—	5·7
40	35·55	6·0010	0·6648	0·9384	− 1·9358	9·81	5·9
80	26·67	4·3970	0·4081	0·6065	− 3·5398	18·69	5·8
120	21·42	3·1263	0·3142	0·5778	− 4·8105	23·94	6·8
			Dark				
0	45·36	7·9368	—	—	—	—	5·7
40	36·97	6·4685	0·4724	0·7182	− 1·4683	8·39	5·7
80	28·89	5·3335	0·2803	0·4597	− 2·6033	16·47	5·4
120	22·64	4·5325	0·2264	0·4018	− 3·6043	21·72	5·2

TABLE 3

50 gms Neem Cake + 50 gms Kans   Av. Temp. 36°C

Period of exposure in days	Total carbon (gms)	Total nitrogen (gms)	NH_3—N (gm)	NO_3—N (gm)	Nitrogen increase (+) or decrease (−) (gms)	Carbon oxidised (gms)	C/N ratio
				Light			
0	42·50	4·3092	—	—	—	—	9·8
40	33·79	5·0217	0·2842	0·3736	+ 0·7125	8·71	6·7
80	25·68	5·4167	0·3742	0·5141	+ 1·1075	16·82	4·7
120	21·47	5·0325	0·3014	0·4937	− 0·3842	21·03	4·0
				Dark			
0	42·50	4·3092	—	—	—	—	9·8
40	35·83	4·8392	0·2460	0·2863	+ 0·5300	6·67	7·4
80	27·69	5·1480	0·3024	0·4183	+ 0·8748	14·81	5·3
120	23·75	4·9631	0·2894	0·3826	− 0·1849	18·75	4·6

TABLE 4

50 gms Neem Cake + 50 gms Kans + 0·5% P_2O_5 as T. B. S.

Period of exposure in days	Total carbon (gms)	Total nitrogen (gms)	NH_3—N (gm)	NO_3—N (gm)	Nitrogen increase (+) or decrease (−) (gms)	Carbon oxidised (gms)	C/N ratio
				Light			
0	42·50	4·3092	—	—	—	—	9·8
40	28·39	5·3493	0·3394	0·5514	+ 1·0331	14·11	5·3
80	20·65	5·8605	0·4846	0·7109	+ 1·5513	21·85	3·5
120	17·76	5·6248	0·4227	0·6927	− 0·2357	24·74	3·1
				Dark			
0	42·50	4·3092	—	—	—	—	9·8
40	30·89	5·0891	0·3012	0·3604	+ 0·7799	11·69	6·3
80	23·86	5·3965	0·3865	0·4769	+ 1·0873	18·64	4·4
120	20·92	5·2793	0·3364	0·4327	− 0·1172	20·58	3·9

TABLE 5

50 gms Neem Cake + 50 gms Kans + 0·5% P_2O_5 as B.B.S.

Period of exposure in days	Total carbon (gms)	Total nitrogen (gms)	NH_3—N (gm)	NO_3—N (gm)	Nitrogen increase (+) or decrease (−) (gms)	Carbon oxidised (gms)	C/N ratio
				Light			
0	42·50	4·3092	—	—	—	—	9·8
40	28·14	5·3518	0·3407	0·5537	+ 1·0426	14·36	5·2
80	20·22	5·8745	0·4875	0·7145	+ 1·4653	22·28	3·4
120	17·34	5·6334	0·4238	0·6936	− 0·2411	25·16	3·0
				Dark			
0	42·50	4·3092	—	—	—	—	9·8
40	30·36	5·0908	0·3047	0·3632	+ 0·7816	12·14	5·9
80	23·42	5·4013	0·3884	0·4783	+ 1·0921	19·08	4·3
120	20·48	5·2784	0·3352	0·5335	− 0·1231	22·02	5·8

TABLE 6

50 gms Neem Cake + 50 gms Kans + 0·5% P₂O₅ as Superphosphate

Av. Temp. 36°C

Period of exposure in days	Total carbon (gms)	Total nitrogen (gms)	NH₃—N (gm)	NO₃—N (gm)	Nitrogen increase (+) or decrease (−) (gms)	Carbon oxidised (gms)	C/N ratio
Light							
0	42·50	4·3092	−	−	−	−	9·8
40	29·46	5·1983	0·3175	0·4052	+0·8891	13·04	5·6
80	22·32	5·7263	0·4498	0·6426	+1·4171	20·18	3·9
120	18·84	5·6124	0·3684	0·6235	− 0·1139	23·66	3·3
Dark							
0	42·50	4·3092	−	−	−	−	9·8
40	31·94	5·0028	0·2921	0·3502	+0·6936	10·56	6·3
80	25·12	5·4659	0·3784	0·5007	+1·1547	17·38	4·5
120	22·23	5·3975	0·3429	0·4868	− 0·0664	20·27	4·1

TABLE 7

100 gms groundnut cake + 40% Moisture (control)

Light							
0	39·40	5·7846	−	−	−	−	6·8
40	29·71	4·4261	0·3284	0·5312	− 1·3585	9·69	6·7
80	22·52	3·2857	0·2196	0·3128	− 2·4989	16·88	6·8
120	20·23	2·9647	0·2024	0·3053	− 2·8199	19·17	6·7
Dark							
0	39·40	5·7846	−	−	−	−	6·8
40	31·62	4·7887	0·2864	0·4127	− 0·9959	7·78	6·6
80	25·26	3·9182	0·2349	0·2848	− 1·8664	14·14	6·4
120	22·68	3·4261	0·1924	0·2785	− 2·3626	16·72	6·6

TABLE 8

50 gms groundnut cake + 50 gms Kans

Light							
0	39·52	3·2331	−	−	−	−	12·2
40	31·55	3·8279	0·1946	0·2953	+0·5948	7·97	8·2
80	23·70	4·1222	0·2463	0·3679	+0·8891	15·82	5·7
120	21·24	4·0018	0·2134	0·3248	− 0·1204	18·28	5·3
Dark							
0	39·52	2·2331	−	−	−	−	12·2
40	23·35	3·6932	0·1536	0·2525	+0·4591	7·17	8·7
80	26·75	3·9573	0·1847	0·3218	+0·7242	12·77	6·7
120	23·58	3·8427	0·1722	0·3027	− 0 1095	15·94	6·1

TABLE 9

50 gms groundnut cake + *50 gms Kans* + *0·5% P_2O_5 as T.B.S.*   Av. Temp. 36°C

Light							
0	39·52	3·2331	—	—	—	—	12·2
40	26·52	4·0866	0·2794	0·3867	+0·8535	13·00	6·4
80	19·48	4·5328	0·3927	0·6274	+1·2997	19·68	4·3
120	17·04	4·3624	0·3618	0·6057	−0·1740	22·48	3·9
Dark							
0	39·52	3·2331	—	—	—	—	12·2
40	29·13	3·9157	0·2034	0·3056	+0·6826	10·39	7·4
80	22·76	4·2483	0·2953	0·3930	+1·0152	16·76	5·3
120	20·08	4·1763	0·2657	0·3758	−0·0720	19·44	4·9

TABLE 10

50 gms groundnut cake + *50 gms Kans* + *0·5% P_2O_5 as B.B.S.*

Light							
0	39·52	3·2331	—	—	—	—	12·2
40	26·25	4·0945	0·2816	0·3928	+0·8614	13·27	6·4
80	19·53	4·5826	0·3985	0·6319	+1·3495	19·99	4·2
120	16·86	4·3518	0·3624	0·6164	−0·2308	22·66	3·8
Dark							
0	39·52	2·2331	—	—	—	—	12·2
40	29·00	3·9262	0·2052	0·3073	+0·6931	10·52	7·4
80	22·44	4·2532	9·4985	0·3945	+1·0201	17·08	5·2
120	19·75	4·1822	0·2694	0·3768	−0·0710	18·77	4·7

TABLE 11

50 gms groundnut cake + *50 gms Kans* + *0·5% P_2O_5 as superphosphate*

Light							
0	39·52	3·2331	—	—	—	—	12·2
40	27·66	3·9864	0·2638	0·4660	+0·7533	11·86	6·9
80	20·04	4·3970	0·3874	0·5586	+1·1639	19·48	4·6
120	18·35	4·1847	0·3465	0·5427	−0·2123	21·17	4·3
Dark							
0	39·52	3·2331	—	—	—	—	12·2
40	29·84	3·8183	0·2034	0·2662	+0·5852	9·68	7·8
80	24·11	4·1480	0·2957	0·3306	+0·9149	15·41	5·8
120	21·73	4·0254	0·2629	0·3154	−0·1226	17·79	5·3

TABLE 12

100 gms castor cake + *40% moisture (control)*

Light							
0	43·08	4·7890	—	—	—	—	8·9
40	32·22	3·7210	0·2837	0·4047	−1·068	10·86	8·6
80	24·42	2·7780	0·1978	0·2989	−2·011	18·66	8·7
120	21·36	2·5430	0·1685	0·2758	−2·246	21·72	8·3
Dark							
0	43·08	4·7890	—	—	—	—	8·9
40	34·77	4·0080	0·2163	0·3488	−0·781	8·31	8·6
80	27·87	3·2850	0·1687	0·2257	−1·504	15·21	8·4
120	24·59	3·0480	0·1534	0·2183	−1·741	18·49	8·0

TABLE 13

50 gms Castor cake + 50 gms Kans Av. Temp. 36°C

Light

0	40·36	3·0762	—	—	—	—	13·1
40	32·05	3·6053	0·2043	0 2427	+0·5291	8·31	8·8
80	24·91	3·8914	0·2634	0·3324	+0·8152	15·35	6·4
120	21·94	3·6742	0·2562	0·3284	− 0·2172	18·42	5·9

Dark

0	40·36	3·0762	—	—	—	—	13·1
40	34·71	3·4853	0·1578	0·2116	+0·4091	5·65	9·9
80	28·12	3·5968	0·2007	0·2967	+0·5206	12·24	7·8
120	25·62	3·4654	0·1906	0·2824	− 0·1314	14·74	7·3

TABLE 14

50 gms castor cake + 50 gms Kans + 0·5% P_2O_5 as T.B.S.

Light

0	40·36	3·0762	—	—	—	—	13·1
40	27·51	3·8668	0·2864	0·3168	+0·7906	12·85	7·1
80	19·17	4·2820	0·3456	0·4808	+1·2058	20·19	4·4
120	17·23	4·1214	0·3175	0·4517	− 0·1606	23·13	4·1

Dark

0	40·36	3·0762	—	—	—	—	13·1
40	29·46	3·6945	0·1976	0·2457	+0·6183	10·90	7·9
80	23·29	3·9990	0·2765	0·3233	+0·9228	17·07	5·8
120	20·46	3·8864	0·2384	0·3083	− 0·1164	19·90	5·2

TABLE 15

50 gms castor cake + 50 gms Kans + 0·5% P_2O_5 as B.B.S.

Light

0	40·36	3·0762	—	—	—	—	13·1
40	27·14	3·8758	0·2912	0·3227	+0·7999	13·22	7·0
80	18·83	4·3142	0·3483	0·4912	+1·2380	21 53	4·3
120	17·00	4·1658	0·3282	0·4632	− 0·1454	23 36	4·0

Dark

0	40·36	3·0762	—	—	—	—	13·1
40	29·08	3·7036	0·2106	0·2483	+0·6274	11·28	7·8
80	22·92	4·0112	0·2834	0·3318	+0·9550	17·44	5·7
120	20·22	3·9642	0·2416	0·3094	− 0·0470	20·14	5·1

TABLE 16

50 gms castor cake + 50 gms Kans + 0·5% P_2O_5 as superphosphate

Light

0	40·36	3·0762	—	—	—	—	13·1
40	28·50	3·7658	0·2528	0·3133	+0·6896	11·86	7·5
80	20·73	4·1612	0·3179	0·4532	+1 0850	19·63	4·9
120	18·14	3·9262	0·2952	0·4228	− 0·2351	20·22	4·5

Dark

0	40·36	3·0762	—	—	—	—	13·1
40	30·88	3·6084	0·1819	0·2320	+0·5322	9·48	8·5
80	14·38	3·8211	0·2386	0·3193	+0·7449	15·98	6·1
120	22·12	3·7346	0·2046	0·3036	− 0·0865	18·24	5·9

Discussion

The foregoing experimental results show that nitrogen rich materials like oil cakes, when composted alone, undergo a loss of nitrogen. The loss of nitrogen from the exposed sets is always higher than that of the covered ones. The rate of loss of nitrogen is rapid in the beginning but slows down with the lapse of time. Dhar and co-workers have advanced a satisfactory explanation for these heavy losses of nitrogen. When the nitrogenous fertilizers or substances containing proteins, such as oil cakes, undergo oxidation under aerobic conditions, the following changes take place :

$$\text{Proteins} \rightarrow \text{Amino acids} \xrightarrow{+O_2} NH_3 \xrightarrow{+O_2} NO_2 \xrightarrow{+O_2} NO_3$$

$$NH_4NO_2 = N_2 + 2H_2O + 718 \text{ K. Cals.}$$
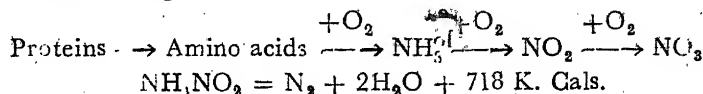
In these processes the unstable substance, ammonium nitrite, is formed as an intermediate product and undergoes oxidation and decomposition aided by light as follows :

(i) $2NH_4NO_2 + O_2 = 2NH_4NO_3$
(ii) $NH_4NO_2 \quad = N_2 + 2H_2O + 718$ K. Cals.
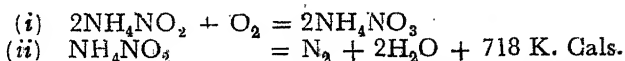
The second chemical change is more prominent than the first and, hence, there is considerable loss of nitrogen ranging from 26·4% to 60·5% in light as is evident from the results given below :

| | | Loss of nitrogen (gms) | |
Treatments	Days	Light	Dark
(i) Neem cake	120	4·8105	3·6043
(ii) Castor cake	120	2·2460	1·7410
(iii) Groundnut cake	120	2·8199	2·3626

But, when 50% organic matter as KANS is added to the oil cakes undergoing decomposition, the loss of nitrogen is highly retarded as is shown in the following table :

| | | Loss of nitrogen (gms) | |
Treatments	Days	Light	Dark
(i) Neem cake + KANS	120	0·3842	0·1849
(ii) Caster cake + KANS	120	0·2172	0·1314
(iii) Groundnut cake + KANS	120	0·1208	0·1095

But. when phosphates are added along with organic matter to the oil cakes, there is marked decrease in nitrogen loss and also there is fixation of atmospheric nitrogen. The retarding effect of these phosphate may be explained by the view point that during the process of ammonification and nitrification of proteins, a highly unstable intermediate compound is formed, that is ammonium nitrite. Due to oxidation of these compounds, the amount of proteins and, consequently, nitrogen in the composts, lowers down. But, due to the presence of these phosphates, more, or less stable phosphoproteins are formed. These compounds seem to resist ammonification and nitrification, and, the loss of nitrogen is checked better.

It is well known that decomposition of ammonium nitrite is accelerated by the presence of the acids. When these oil cakes undergo oxidation, some acids are likely to be produced which accelerate the decomposition of ammonium nitrite leading to the loss of nitrogen. But, in the presence of phosphates, which

act as buffer due to the fact that second and third dissociation constants of phosphoric acid are small, the increase in the H ions concentration of the system is not possible.

The effect of KANS in retarding the loss of nitrogen seems due to the fact that KANS is a carbonaceous material and acts as a negative catalyst and in this way checks the oxidation of proteins in the oil cakes. It is well known that carbohydrates preserve body protein from undergoing oxidative deamination. It seems, therefore, that KANS also behaves in a similar manner in the oil cake composts, and preserves their protein from being oxidised and thus lost.

As phosphates markedly increase nitrogen fixation and since the observed loss is a balance of total nitrogen losses occurring and nitrogen fixation going on side by side, the phosphates behave as agent in checking the nitrogen loss. Dhar and Biswas[7] found that when oil cakes are composted alone, there is appreciable loss of nitrogen, but, as soon as molasses is added, instead of a loss of nitrogen from the oil cake composts, there was fixation of atmospheric nitrogen. Dhar and Agrawal[8] have found a marked loss of nitrogen when oil cake alone is added to the soil, but, as soon as coal were added, they decreased the nitrogen loss.

Dhar and Mukherji[9] have explained the checking of this loss of nitrogen by organic matter from the view point of negative catalysis as the retarding influence of an easily oxidisable substance upon the oxidation of other substances. They have observed as follows :

"Both carbohydrates and fats act as a negative catalysts and retard the oxidation of aminoacids and proteins, and, that is way carbohydrates and fats are likely to act as proteins sparess in the animal body. Similarly, the oxidation of carbohydrates and fats is also retarded by proteins and amino acids." These results have been confirmed by Ghosh and Rakshit[10].

Mukherji and Agrawal[11], from their field experiments at Kanpur, have obtained favourable results for both wheat and sugarcane with SANAI (Sun-hemp) as green manure. They have shown that addition of green manure to oil cakes or ammonium sulphate leads to marked incraase in the yield of wheat as compared with that obtained with green manure alone or the artificials alone.

Thus, my experiments reveal the fact that the loss of nitrogen, which is found in the nitrification of protein–rich organic materials, can be checked by the incorporation of KANS and Phosphates in the soil.

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Possibilities of using microorganisms as seed inoculants for increasing crop production

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Summary

The problem of providing food to the nation is intimately connected with providing adequate proteins as its shortage in under-developed countries is acute. It is necessary, therefore to meet this through the production of pulses of high protein content and through feeding the cattle with leguminous fodder of high protein value. In this connection there is an immediate need to examine the present position regarding the type of *Rhizobium* strains that are now prevalent in different areas under leguminous food and fodder crops. Investigations carried out so far revealed that the yields of these crops have been considerably low because of the poor quality of *Rhizobium* strains in these areas and inadequate supply of water and nutrients. Effective strains of *Rhizobium* have been isolated and after due testing are now being maintained at the IARI and a few other laboratories in the country for over 20 leguminous food and fodder crops. There is an urgent need to product these cultures on a mass scale in order to distribute them to the cultivators growing food and fodder crops. It has been observed that the specificity of the *Rhizobium* strains in cases like pea, soybean and groundnut is closely linked up not only with a species but also with the variety of the crop in the particular species. Therefore careful investigation is essential to select the *Rhizobium* strains suited to the high yielding varieties of legumes that are being introduced in this country.

Even in U.S.A. where 4 million tons of nitrogen in the form of artificial fertilizers are produced, approximately 42% of the legume seeds planted each year are inoculated. It is therefore essential and prudent to make the maximum use of nitrogen available in the atmosphere which can be harnessed for increased production of legumes through seed inoculation in this country followed by suitable soil amendments especially that of addition of phosphates, boron and molybdenum wherever necessary and correcting for acidity through lime. This will facilitate the diverting of nitrogenous fertilisers which are scarce to the cereal crops.

The use of *Azotobacter* and phosphorus solubilising organisms has been found to result in increasing yields of cereal crops in specific cases. Carefully conducted experiments using radioactive isotopes P^{32} showed that seed inoculation with phosphorus solubilising organisms results in increased uptake of phosphate from tricalcium phosphate. The potentiality of these organisms needs to be exploited, for increasing the solubility of phosphates available in indigenous basic slag and rockphosphate. Evidence is accumulating that the use of bacterial inoculant is more effective in soils of high fertility or when manures and fertilisers have been applied showing thereby that the contribution of these inoculants may be through synthesis of growth promoting substances. The use of microorganisms as seed inoculant is recommended for increasing crop production in order to increase the beneficial effects of added manures and fertilisers and thereby enhance crop production.

The problem of providing food to the nation is mainly a question of provid-ing adequate proteins as its shortage in underdeveloped countries is very acute. Nearly 1/4th of India's population are under 15 years of age and as such the need for proteinous food rich in amino acids for their nutrition and development is essential. Obviously one means of achieving this is through the production of pulses of high protein content and through feeding the cattles with fodder of high protein value. In this country, about 24 million hectares of land are under the cultivation of pulse crops and about 6 million hectares of land are under fodder crops. In table 1 are shown the extent of area covered by pulse crops and the average yields per hectare.

From this it can be seen that the yields are rediculously low and there is vast scope in increasing the yields of the pulse crops as well as the pulse protein that can be obtained through proper manuring and inoculating the seeds with efficient strains of Rhizobium. In Table 2, the percentage increases in yields and percentage increase in the nitrogen removed by the crop that were attained in some of the experiments are recorded.

Effective strains of *Rhizobium* are now being maintained at the IARI and a few other laboratories in the country for about 20 leguminous food and fodder crops, listed below.

Legumes Commonly Grown in India

1.	Berseem	*Trifolium alexandrinum*
2.	Black gram, urid	*Phaseolus mungo*
3.	Cluster bean, Guar	*Cyamopsis tetragonoloba*
4.	Cowpea	*Vigna sinensis*
5.	Dhaincha	*Sesbania aculeata*
6.	Fenugreek, Methi	*Trigonella foenum-graecum*
7.	Gram	*Cicer arietinum*
8.	Green gram (Mung)	*Phaseolus aureus*
9.	Groundnut or peanut	*Arachis hypogea*
10.	Khesari	*Lathyrus sativum*
11.	Lablab (Country bean)	*Dolichos lablab*
12.	Lucerne	*Medicago sativa*
13.	Pea	*Pisum sativum*
14.	Pillipesara	*Phaseolus tribus naripavarn*
15.	Red gram or pigeon pea, arhar or rahar	*Cajanus cajan*
16.	Soybean	*Glycine max*
17.	Senji	*Mililotus indica*
18.	Sunhemp	*Crotalaria juncea*
19.	Horse gram	*Dolichos biflorus*

In some of the field trials conducted in different parts of the country with *Rhizobium* cultures isolated at the IARI or at the State laboratories clearly demonstrated the efficiency of the strains. In tables 3 and 4 are recorded the total number of field experiments conducted with different strains and the number of experiments showing significant increase are given.

So far as the experiments in the Madras state are concerned, they related to strains maintained in the state and experiments conducted in the previous years

by the State Investigators. From the above, the possibilities of increasing the protein supply from each acre to the population through increasing yield of leguminous crops is indicated and as such there is an immediate need to multiply the cultures on a mass scale and supply to the cultivators. But in areas where phosphate and molybdenum are deficient and the soil is acid, these elements are to be supplied and acidity is to be corrected through the application of lime. The use of *Rhizobium* inoculants which cost only about Rs. 5 for quantities required per hectare would definitely lead to increase the availability of protein food to the human and cattle population, and the nitrogenous fertilizers, to a great extent be diverted to cereal crops. Recently evidence has been obtained that specificity of the *Rhizobium* strains in cases like soybean is closely linked up not only with the species but also with the variety of the crop in the particular species. Therefore, investigation is essential to select the *Rhizobium* strains suited to the high yielding varieties of legumes that are being introduced in this country.

It may be mentioned that in the U.S.A. where the production of artificial nitrogenous fertilisers amounted to 4 million tons of nitrogen, approximately 42 per cent of the legume seeds planted each year are inoculated. It is therefore prudent and essential to make the maximum use of nitrogen of the atmosphere which can be harnessed for increasing the production of legumes through seed inoculation in this country followed by suitable soil amendments.

The use of *Azotobacter* and phosphorus solubilising organisms has been found to result in increasing yields of cereal crops in specific cases. The number of experiments conducted in India with *Azotobacter* and the number of experiments showing positive response are given in table 5.

The one point that is frequently disputed in the case of *Azotobacter* inoculation is whether this organism can be introduced and stabilised near the rhizosphere of agricultural crops. The investigations carried out at the IARI showed that under specific conditions namely after addition of large amount of organic matter and the application of superphosphate, the organism can be established near the rhizosphere.

Rhodopseudomonas capsulatus and *Azotobacter* treatments result in an abundant establishment of the latter near the rhizosphere of the wheat crop. Besides being a nitrogen fixer *Azotobacter* also synthesises growth promoting substances like biotin, pantothenic acid, folic acid, indole acetic acid and substances similar to gibberellin. Experiments conducted at Cuttack showed that when the soil was supplied with nitrogenous and phosphatic fertilisers, the seed treatment with *Azotobacter* increased the yield of paddy (Table 6).

It may however be mentioned in some of the experiments, the response to *Azotobacter* inoculation was not significant. This might be due to the fact that either the soil was very deficient in organic matter or phosphate or adequate inoculum was not applied or the soil already contained sufficient *Azotobacter* population or soil acidity was not corrected or the crop needed much more nitrogen than is made available through *Azotobacter* in the treatments where fertilizers other than nitrogenous was added.

Carefully conducted experiments using radioactive isotopes P^{32} showed that the seed inoculation with phosphorus solubilising organisms resulted in increasing the uptake of phosphate from tricalcium phosphate by the crop (Table 7).

There is need to exploit the potentiality of organisms for increasing the solubility of phosphate available in indigenous basic slag and rock-phosphate.

It may also be pointed out that the treatment of the leguminous seeds with phosphorus solubilising organisms and supplying phosphates to the soil in a relatively insoluble form like bonemeal or rockphosphate leads to not only better supply of phosphorus to the crop but also better uptake of nitrogen (Tables 8, 9 and 10).

Evidence is accumulating that the use of bacterial inoculants is more effective when manures and fertilizers have been applied showing thereby that the contribution of these inoculants may be through synthesis of growth promoting substances. The use of these bacterial inoculants is therefore recommended for increasing the crop production and for conserving the available fertilizers and use them over wider areas in view of the better availability of nutrients present in these fertilisers to crops when the seeds are treated with bacterial inoculants.

TABLE 1

Area and Production of Pulses

State	Area in acres $\times 10^6$	Production in tons $\times 10^6$
Uttar Pradesh	10·58	2·00
Madhya Pradesh	5·70	0·94
Bihar	5·43	1·04
Andhra Pradesh	4·81	0·40
Bombay	3·28	0·40
Madras	2·84	0·22
Punjab	2·72	0·64
Rajasthan	2·52	0·33
Madhya Bharat	2·19	0·20
West Bengal	1·55	0·39
P. E. P. S. U.	1·20	0·30
Orissa	0·92	0·22
Mysore	0·92	0·06
Vindhya Pradesh	0·85	0·13
Other States	1·08	0·14
Total	46·69	7·51

1954-65 Ttoal area under pulses......58·73 × 10^6 acres
or 23·77 × 10^6 hectares

TABLE 2

	Legume inoculation		% age increase in yield	% age increase in nitrogen removed by the crop
1.	Berseem	(*Trifolium alexandrinum*)	133	129
2.	Lucerne	(*Medicago sativa*)	35	38
3.	Soybean	(*Glycine max*)	45	60
4.	Urid	(*Phaseolas mungo*)	46	26
5.	Sem	(*Dolichos lablab*)	133	100
6.	Peas	(*Pisum sativum*)	39	26
7.	Gram	(*Cicer arielinum*)	58	47
8.	Cowpeas	(*Vigna sinensis*)	23	33
9.	Arhar	(*Cajanas cajan*)	76	–
10.	Guar	(*Cyamopsis tetragonoloba*)	100	90

TABLE 3*
Rhizobium inoculation experiments conducted
Field Experiments

Place	Crop	No. of field experiments conducted	Significant increase in field expt.
Bihar State			
Kanke	Soybean	2	2
	Mung	3	3
	Urid	1	1
Parmia	Gram	3	1
	Khesari	3	1
	Kalai	3	—
	Pea	1	1
Sabeen	Soybean	3	2
Patna	Gram	2	—
Bakraganj	Pea	1	1
	Rhizobium inoculation†		
Madras State	Sunhemp	1	1
	Rahar	1	1
	Cowpea	1	1
	Green gram	1	—
	Black gram	1	—

* Communication from Dr. K. K. Jha.
† Communication from Madras State Department of Agriculture.

TABLE 4†
Rhizobium inoculation tests with Soybean, Urid and Cowpea
Field Experiment, Kanpur

Crop	Treatment	Yield of grains (Kg/hectare)	Increase over control (%)
Urid	Uninoculated	1775	—
	Inoculated	1950	10
	Uninoc. + P_{45}*	1825	—
	Inoc. + P_{45}	2090	15
Soybean	Uninoculated	950	—
	Inoculated	1088	15
	Uninoc. + P_{45}	1320	—
	Inoc. + P_{45}	1808	36
Cowpea	Uninoculated	1775	—
	Inoculated	1650	7
	Uninoc. + P_{45}	3180	—
	Inoc. + P_{45}	3270	3

* Superphosphate at 45 Kg. P_2O_5 per hectare.
†Data of Dr. B. K. Mukherjee.

TABLE 5

Inoculation with Azotobacter

	Field trials		No. of experiments showing significant increase
Delhi			
Alluvial soil	Wheat	3	Nil
	Peas	3	1
	Cabbage	1	1
Cuttack	Paddy	2	2
Anand	Jowar	3	2
Hyderabad	Paddy	1	1
		13	7

TABLE 6*

Experiment with Azotobacter in under upland conditions (C. P. R. I.)

Cuttack Field Experiment.   (Unpublished Data)

Yield of grain in Kg/HA   (Var. Paddy PTB 10)

Treatments	1959–60	1960–61	Mean
M_0T_0	1170	2028	1599
M_0T_1	1187	1856	1522
M_1T_0	1494.	2107	2051
M_1T_1	2520	2311	2415
M_2T_0	1318	1996	1657
M_2T_1	1325	2130	1728
		C.D. (0·05)	117

M_0 – Unmanured control

M_1 – 30 lb N/AC as amm. sulph + 30 lb P_2O_5/AC as superphos.

M_2 – 30 lb P_2O_5/AC as superphos. + 30 lb K_2O/AC as potash sulph.

T_0 – Uninoculated

T_1 – Inoculated

Experiment conducted in collaboration with C. R. R. '. Cuttack.

* Sundara Rao, W. V. B. (1964).   Nati·nal Institute of Science.   Symnosium on Fertility of Indian soils, Madras (196?).

TABLE 7

Utilisation of added P_2O_5 by wheat (1964–65) as percent

(Mean of @ Replications)

Utilisation of added P_2O_5

Treatment	With FYM		Without FYM	
	S_1	S_2	S_3	S_4
(1) Uninoculated control	6·81	4·24	6·66	4·96
(2) Inoculated with P. B	8·92	5·31	7·70	6·67
(3) Inoculated with I_2	8·18	5·51	8·87	7·09
'F' test	Sig.	Sig.	Sig.	Sig.
SEm ±	0·533	0·533	0·533	0·533
C. D. at 5% ±	1·53	1·53	1·53	1·53

S_1 = Soil + FYM. + Amm. Sulph. + Super.
S_2 = Soil + FYM + Amm. Sulph. + Apatite.
S_3 = Soil + Amm. Sulph. + Super.
S_4 = Soil + Amm. Sulph. + Apatite.

Sundara Rao. W. V. B. and Bajpai, P. D. (1966).
"Isotopes in Agriculture" Seminar organised by the ICAR at New Delhi.

TABLE 8

Total P_2O_5 uptake by cowpea in mg/pot as affected by inoculation

(Mean of 4 replications)

Inoculation	With FYM				Without FYM			
	S_1		S_2		S_3		S_4	
	Total P_2O_5 uptake	% increase	Total P_2O_5 uptake	% increase	Total P_2O_5 uptake	% increase	Total P_2O_5 uptake	% increase
(1) Uninoculated control	38·71	–	38·62	–	43·33	–	42·51	–
(2) Inoculated with P. B.	54·64	41·15	50·45	30·63	63·30	46·09	48·78	14·75
(3) Inoculated with I_2	50·60	30·72	52·20	35·16	48·03	10·85	45·98	8·16
'F' test*	Sig.		Sig.		Sig.		Sig.	
SEm ±	2·825		2·825		2·825		2·825	
C. D. at 5% ±	8·06		8·06		8·06		8·06	

S_1 = Soil + FYM + Super.
S_2 = Soil + FYM + Apatite.
S_3 = Soil + Super.
S_4 = Soil + Apatite.

Sundara Rao, W. V. B. and Bajpai, P. D. (1966).
"Isotopes in Agriculture", Seminar organised by ICAR at New Delhi.

TABLE 9

Nitrogen uptake by cowpea in mg/pot as affected by inoculation

(Mean of @ replications)

	With FYM				Without FYM			
	S_1		S_2		S_3		S_4	
	N uptake	% increase	N uptake	% increase	N uptake	% increase	N uptake	% increase
(1) Uninoculated control	188·42	–	147·35	–	155·11	–	166·85	–
(2) Inoculated with P. B.	208·25	11·00	201·79	37·00	228·50	47·31	195·48	17·16
(3) Inoculated with I_2	190·71	6·00	215·02	45·00	211·98	36·66	193·72	16·10
'F' test	Sig.		Sig.		Sig.		Sig.	
SEm ±	9·910		9·910		9·910		9·910	
C. D. at 5% ±	24·14		24·14		24·14		24·14	

S_1 = Soil + FYM + Super. S_3 = Soil + Super.
S_2 = Soil + FYM + Apatite. S_4 = Soil + Apatite.

Sundara Rao, W. V. B. and Bajpai, P. D. (1966).
"Isotopes in Agriculture" Seminar organised by the ICAR at New Delhi.

TABLE 10

(Field experiment—Delhi soil) (Unpublished)

Nitrogen uptake by Berseem (1963·64) as affected by inoculation

Treatment	Nitrogen uptake by Berseem in g./plot (mean of 4 replications)
	Total of all cuttings (pooled)
A. No manure	1324
B. P. B.	1596
C. I_2	1382
D. FYM	1484
E. (D) + P. B.	1935
F. (D) + I_2	1795
G. Super	1920
H. Super + P. B.	1989
I. Super + I_2	2363
J. FYM + Super	2340
K. (J) + P. B.	2623
L. (J) + I_2	2443
M. FYM + rockphosphate	1487
N. (M) + P. B.	1983
P. (M) + I_2	1849
'F' tast*	Sig.
SEm ±	167·9
C. D. at 5% ±	479

(Joint field experiments by the Division of Microbiology and Agronomy, I.A.R.I. New Delhi).

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